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## **Topic 1**

# **Ionic Liquids, Liquid Metals**

## Solid Liquid Equilibria and Molecular Modeling Predictions of Glucose in Tetra Butyl Ammonium Bromide based Deep Eutectic Solvents

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The present work attempts to measure the solid-liquid equilibrium (SLE) of glucose in three novel low cost deep eutectic solvents (DES) namely tetrabutylammonium bromide [TBAB]-Imidazole, [TBAB]-ethylene glycol, and [TBAB]-glycerol over the temperature range 299.15- 353.15 K. The DES are also known as second generation Ionic Liquids. The [TBAB]-Imidazole DES gave a highest solubility (20 mole%) of glucose. The experimental solubility data was then correlated with the local thermodynamic models namely Apelblat equation, NRTL and UNIQUAC models. All the models gave excellent agreement with experimental data. The thermodynamic functions of dissolution such as Gibbs energy, enthalpy and entropy of dissolution were also calculated from the modified van't Hoff equation. The dissolution functions gave positive values for all the studied systems indicating that the process is endothermic in nature while being non-spontaneous and entropically favourable. In addition, classical Molecular Dynamic (MD) simulations were performed to elucidate the nature of glucose-DES non-bonded interactions. From the MD simulations, the anion of hydrogen bond Acceptor (HBA) and the hydrogen bond donor (HBD) molecules are primarily responsible for the dissolution of glucose. The isomerization of glucose to fructose in [TBAB]-Imidazolium DES was observed at a low temperature of 333.15 K which resulted in a lower concentration of glucose at higher temperature.

## A molecular dynamics study for dibenzo-18-crown-6 assisted metal ion extraction in ionic liquid-water biphasic systems

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In this work, we report the molecular dynamics studies on the mechanism of crown ether (CE) assisted cesium ( $\text{Cs}^+$ ) or sodium ( $\text{Na}^+$ ) ion transfer in a hydrophobic IL, 1-Hexyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide [HMIM][Tf<sub>2</sub>N]. The simulations were carried out both in absence and presence of methanol. Thereafter to understand the mechanism of complexation and the behavior of crown ether ligand, crown ether (CE) molecules,  $\text{Cs}^+\text{NO}_3^-$ , and  $\text{Na}^+\text{NO}_3^-$  ions were inserted randomly in the ionic liquid–water biphasic system. It was observed that the addition of a modifier with low dipole moment such as methanol to the aqueous phase has enhanced the stability and extraction efficiency of the complex. The interaction energies during complexation of  $\text{Cs}^+$  and  $\text{Na}^+$  ions with crown ether (DB18C6) were further analyzed. A large RDF peak height suggests a high stability and a strong interaction in the complexed species. The large magnitude of the RDF peak between metal ion and oxygen atom of the crown ether is similar to that obtained by Sahu *et al.*[1] and Maerzke *et al.*[2]. After the complex formation it is very clear that the electrostatic interactions of the metal ion are particularly attractive in nature and are crucial in realizing complexation.

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## Metal ion partitioning with calix[4]arene-benzo-crown-6 in ionic liquid-water biphasic systems

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Cesium is an extensive fission product in spent nuclear fuels. The removal from the nuclear wastes forms a key part of waste remediation strategies. We report the molecular dynamics studies on the interfacial behavior of cesium ( $\text{Cs}^+$ ) or sodium ( $\text{Na}^+$ ) extraction by calix-benzo-crown-6 (CBCBGA) ionophore. For the benchmarking study, the phase separation for [BMIM][Tf<sub>2</sub>N]-water was validated. Thereafter, to understand the mechanism of complexation and the behavior of crown ether ligand, crown ether (CE) molecules and  $\text{Cs}^+\text{NO}_3^-$ , and  $\text{Na}^+\text{NO}_3^-$  ions were inserted randomly in the ionic liquid–water biphasic system. It was observed that the  $\text{Cs}^+$ -CE complex formed during the simulation diffused at a faster rate as compared to  $\text{Na}^+$ -CE complex from the interface to the bulk IL phase. The radial distribution function (RDF), interaction energies and the diffusion coefficient during complexation of  $\text{Cs}^+$  or  $\text{Na}^+$  cation with CBCBGA were also computed. A large RDF peak height suggests a high stability and a strong interaction in the complexed species. The new ionophore is found to be highly selective for  $\text{Cs}^+$  as compared to  $\text{Na}^+$  in the simulated high level liquid waste solution. Within the limited sample size of six crown ethers and ten cesium and sodium nitrate molecules, CBCBGA was able to capture two cesium atom(s) and one sodium atom respectively towards its crown cavity after a 30 ns simulation time. In case of  $\text{Cs}^+\text{NO}_3^-$  system the captured cesium atoms were found to lie towards the bulk IL phase. This work hence summarizes the interface phenomena.

# Selective Thermal Dehydrogenation of Ethylene Diamine Bisborane Facilitated by Phosphonium Based Ionic Liquids

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Ionic Liquids (ILs) made them preferable solvents for solution thermolysis of ethylene diamine bisborane (EDAB) as they are known to stabilize the ionic intermediates formed during dehydrogenation. The very stabilization effects contributes to the enhancement of hydrogen release and suppression of induction time. In this regard, the phosphonium-based cations poses an alternative option for thermal dehydrogenation of EDAB due to its higher thermal stability, which makes them an efficient energy carrier for boranes. Absence of acidic protons in cation is known to enhance the thermal stability of phosphonium ILs in basic and nucleophilic conditions [1],[2],[3]. The ILs are chosen based on the solubility of EDAB in respective ILs as obtained by a-priori COSMO-SAC (Conductor like Screening Model Segment Activity Coefficient) model.

The current work reports the thermal dehydrogenation of ethylene diamine bisborane (EDAB) performed on the COSMO-SAC screened Ionic Liquids namely Trihexyl(tetradecyl) phosphonium bis (2,4,4-trimethylpentyl) phosphinate ([TDTHP][Phosph]) and Trihexyl(tetradecyl) phosphonium dicyanamide. Dehydrogenation experiments were carried out under vacuum and temperatures of 95 and 105 °C. No induction period was observed in dehydrogenation experiment for both IL's. A maximum yield of 3.25 equivalents of hydrogen was obtained with EDAB/[TDTHP][Phosph] at 105 °C. <sup>1</sup>H NMR study confirmed the catalytic role of ILs during dehydrogenation. Further HR-MS analysis of residual products revealed the exact mass of end products. These were corroborated with the formation of oligomeric dehydrogenated EDAB compounds having four and five repeat units which eventually led us in formulating the reaction mechanism.

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# The Internal Pressure and Cohesive Energy Density of Liquid Metallic Elements

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The internal pressures,  $P_{\text{int}} = (\partial U / \partial V)_T$ , of practically all the liquid metallic elements in the Periodic Table up to plutonium (except Pm, Tm, Tc, Np) at their melting points  $T_m$  were calculated from data in the literature [1]. The working equation is  $P_{\text{int}} = T\alpha_P / \kappa_T$ , involving the isobaric expansibility  $\alpha_P$  and the isothermal compressibility  $\kappa_T$  [2], whereas the additional term  $-P$  is negligible at  $T_m$ . The cohesive energy of the liquid metals accounts for all the interactions that take place among the particles present: atoms, ions, and a 'sea' of electrons in the liquid metals. The respective cohesive energy densities,  $ced = -U/V = (\Delta_v H - RT)/V$ , are obtained from literature data for the molar enthalpy of vaporization  $\Delta_v H$  and molar volume  $V$  and have the dimensions of pressure.

The temperature dependence of  $P_{\text{int}}$  to be represented as a second degree power series:  $P_{\text{int}} = a + bT + cT^2$  for the liquid alkali, iron-group, and post-transition metals. They generally lead to flat maxima in the curves of the internal pressure vs. the temperature. A plot of  $\ln(ced/\text{kJ mol}^{-1})$  against  $\ln(V/\text{cm}^3 \text{ mol}^{-1})$  yields the value of  $n = 0.75 \pm 0.13$  for the Frank relationship of  $U/V^n$  for the internal pressure of the liquid metals.

The ratio  $P_{\text{int}}/ced$  for liquid metals is  $0.24 \pm 0.02$ , outliers being Be, Mo, W, and Co. This ratio is compared with those for various liquids that are ranked as follows: molten salts ( $P_{\text{int}}/ced < 0.1$ ) < polar/hydrogen bonded molecular solvents (0.07 for water at ambient conditions, 0.36 for formamide, up to 0.5 for other such liquids) ~ liquid metals < room temperature ionic liquids ( $P_{\text{int}}/ced = 0.75 \pm 0.20$ ) < nonpolar molecular solvents ( $P_{\text{int}}/ced > 1$ ).

The reverse of this list reflects the relative strengths of the mutual interactions of the particles constituting these liquids. Thus, in liquid metals the interactions of the cations imbedded in the 'sea' of conduction electrons are not as strong as in molten salts, where the coulombic interactions between relatively small cations and anions are very strong.

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# Vapour-liquid phase behaviour of ionic fluids in disordered porous media: application of the scaled particle theory and the ion-association concept

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We study the vapour-liquid phase behaviour of size-symmetric and size-asymmetric primitive models of ionic fluids confined in disordered porous matrices formed by uncharged hard spheres (HS) or overlapping hard spheres (OHS). The proposed theoretical approach combines the scaled particle theory and the associative mean-spherical approximation. The theory correctly reproduces the basic effects of porous media on the vapour-liquid phase diagrams of an ionic fluid, i.e. with a decrease of porosity the critical point shifts toward lower fluid densities and lower temperatures, simultaneously the coexistence region is getting narrower. An analysis of the ion association along the vapour-liquid coexistence curves demonstrates a strong dependence on a matrix porosity by causing an increase in the association degree between oppositely charged ions when the porosity is lowering. Also it is observed that at the critical point the association reaches its minimum for the gas phase and the maximum for the liquid phase. It is shown that the critical parameters of both the symmetric and asymmetric ionic fluids confined in the OHS matrix are higher than in the HS matrix at the same porosity. However, it should be noted that the association phenomena appearing between ions are not restricted solely by formation of pairs, but also higher order clusters should be taken into account. Thus, in order to improve a quantitative description of the vapour-liquid transition of ionic fluids we propose a generalization of the developed theory due to which the presence of trimers and tetramers in the ionic system is considered. Finally, the modern theory of associative liquids is applied to study a model of complex ions consisting of charged and neutral groups. This model is used to describe the vapour-liquid phase behaviour of room temperature ionic liquids in the bulk and in disordered porous media.

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## Frenkel line: Theoretical background and experimental evidences

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A liquid near the melting curve has much more in common with a solid than with a gas – this interesting result has been increasingly appreciated recently in the area of liquids, although not widely by physics community in general. For example, a liquid supports transverse collective modes at high frequency that endow the liquid with shear rigidity at that frequency. Many physical properties, including heat capacity, heat conductivity, electroconductivity and so on, change only weakly as a result of melting despite the loss of the long-range order. Close to the melting curve, this behavior is observed at very high pressures and temperatures well above the critical point. To denote this state of the liquid, the term “rigid liquid” was proposed. Recently, we introduced the concept of “Frenkel line” on the pressure-temperature (or density-temperature) phase diagram that separates the state of the rigid-liquid from the dense gas. Crossing the Frenkel line on temperature increase results in the disappearance of shear rigidity at all frequencies, specific heat reaching  $2k_B$ , and, importantly, the qualitative change of temperature dependence of key system properties such as structure factor features, heat capacity, speed of sound, diffusion coefficient, viscosity and thermal conductivity.

Here we present new results of liquid-to-dense gas transition at very high pressures for real fluids such as neon, methane, iron, water, CO<sub>2</sub>. The data of the location of the lines of liquid-to-dense gas transition at supercritical pressures are very important for supercritical technologies.

# Analysis of local bond-orientational order for liquid gallium at ambient pressure

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The static structure factor (SSF) of liquid Ga at ambient pressure (AP), which is well known for exhibiting a shoulder on the high- $q$  side of the first peak, has been observed for nearly half a century [1]. However, resolving its local structure remains a subtle problem in liquid metal researches. In the present study, we investigated local structures of liquid Ga at AP via *ab initio* molecular dynamics (AIMD) simulations.

In terms of the local bond-orientational order (LBOO) parameters, a cluster approach for analyzing local structures of simple fluids was developed [2]. In this approach, a cluster in a liquid is defined as a combination of neighboring seeds and their nearest neighbors, where seeds are particles having at least  $n_b$  local-orientational bonds, and a cluster ensemble is a collection of clusters that are specified with LBOO  $n_b$  and number of seeds. Both  $q_4$  and  $q_6$  LBOO parameters were used to analyze structures of liquid Ga generated by using the VASP code at 323 K, just above the melting temperature ( $T_m = 302$  K). An observation for the AIMD liquid was that particles with low coordination numbers had local structures in higher LBOO of fourfold orientational symmetry. Further, two types of cluster structures were found in the simulated liquids, with one characterized by sixfold orientational symmetry and the other typified with fourfold orientational symmetry. The SSFs of cluster ensembles with sixfold orientational symmetry were akin to the SSF of a hard-sphere fluid. On the contrary, the SSFs of cluster ensembles showing fourfold orientational symmetry behaved similarly as the anomalous SSF of liquid Ga at AP by displaying a high- $q$  shoulder.

We also examined the similarity between the local structures of the AIMD liquid and the structures of multiple Ga solids, including  $\alpha$ -Ga,  $\beta$ -Ga, Ga II and Ga III. First, the ( $q_4$ ,  $q_6$ ) points of these Ga solids were found to be located on the rim of the  $q_4$ - $q_6$  distribution of the AIMD liquid. Secondly, a highly LBOO cluster whose SSF displayed a high- $q$  shoulder had local structures more similar to  $\beta$ -Ga than other Ga solids. Furthermore, the cluster structures exhibiting fourfold orientational symmetry had an inclination to resemble more to the structure of  $\beta$ -Ga.

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# The polymorphic plethora of Wigner bilayer systems

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We consider an ensemble of mobile point charges (nominal charges  $-e$ ), immersed in a dielectric medium and confined between two parallel plates, which are separated by a distance  $\eta$  and which bear uniform charge densities  $\sigma_1 e$  and  $\sigma_2 e$ , with the asymmetry parameter  $A = \sigma_2 / \sigma_1$ . Combining complementary theoretical approaches (i.e., analytical calculations, numerical optimization techniques based on evolutionary algorithms) we provide at vanishing temperature a comprehensive diagram of ordered ground state configurations of the charges as we systematically vary the asymmetry parameter  $A$  and the plate separation  $\eta$  [1]. The complex interplay between commensurability requirements between the ordered structures on each of the layers, on one side, and the quest for local charge neutralization, on the other side, leads to a plethora of exotic Wigner bilayer configurations: among those are Archimedean tilings or pentagonal structures, both of which can be considered as precursors of quasi-crystalline structures. Complementary Monte Carlo simulations, carried out at small, but finite temperatures provide evidence of the thermal stability of the predicted structures. In addition, the system comes up with other unexpected features, such as long-range attractions between the plates, the appearance of macroscopic charges, or the emergence of non-conventional phase transitions, pertaining to different universality classes. Our investigations demonstrate that even in a simple system the emergence of complex structures can easily be triggered via a systematic variation of two external parameters (in our case  $A$  and  $\eta$ ).

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# Influence of alkyl chain length on the diffusion of a nitroxide radical in imidazolium-based ionic liquids

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Solutions of a nitroxide radical in imidazolium-based ionic liquids with different alkyl chain length were studied by electron paramagnetic resonance (EPR) spectroscopy. The radical was perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (pDTEMPONE) and the ionic liquids were four members of the 1-alkyl-3-methylimidazolium tetrafluoroborate family ( $[C_n\text{mim}][\text{BF}_4]$ ) with ethyl ( $n=2$ ), butyl ( $n=4$ ), hexyl ( $n=6$ ), and octyl ( $n=8$ ) groups. The EPR spectra of solutions with various radical concentrations were recorded at temperatures between 0°C and 120°C.

The EPR spectra were fitted to the spectral function obtained from the modified Bloch equations for the magnetization of radicals. The fitted values of EPR parameters that quantify spin dephasing, coherence transfer and hyperfine splitting were analyzed as functions of radical concentration at each measured temperature. Using linear fitting, we determined linear concentration coefficients of these EPR parameters. The concentration coefficients are affected by the relative motion of radicals, which modulates the Heisenberg spin exchange and dipole-dipole interactions between radicals. Assuming continuous diffusion of radicals, the diffusion coefficients of pDTEMPONE were calculated from the concentration coefficients by numerical solving of the kinetic equations for the spin evolution of the interacting radical pair [1].

Upon lowering the temperature, the calculated diffusion coefficients of pDTEMPONE in all ionic liquids decrease slower than is predicted by the Stokes-Einstein relation and slower than its rotational diffusion coefficient [2]. Such behavior of tracer diffusion was detected in supercooled liquids and ascribed to the presence of dynamical heterogeneities. Radical diffusion was compared to self-diffusion of ions in these ionic liquids measured by NMR [3,4,5]. We found that the diffusion coefficient of the radical and ions are similar for short alkyl length ( $n=2$ ) and that the diffusion coefficient of the radical decreases much slower than that of ions with increasing alkyl chain length. This relative enhancement of radical diffusion with the lengthening of alkyl chain might be related to the aggregation of the alkyl chains with  $n \geq 4$  in non-polar domains [6]. The fast diffusion of a neutral tracer through these soft non-polar domains [7] can increase its effective diffusion coefficient relative to that of original ions.

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# The influence of multivalent ions on charge-regulation interaction

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One of the biggest discoveries in the colloidal science is certainly the exotic phenomenon of like-charge attraction arising between same-charged macromolecules in a multivalent ion solution. Although it was firstly observed in simulation [1] back in 1984, and soon after confirmed in experiments, the proper theoretic explanation came two decades later, when the so-called field-theoretic approach to Coulomb fluids was developed. Its advantage reflects in the fact that the framework provides a consistent description of weakly charged systems, as well as it describes the systems where the strong ion correlation dominate [2]. Nevertheless, it is restricted to macromolecules bearing the fixed surface charge and fails to describe systems dependent on acid/base equilibrium, such as proteins. In those systems, where the charge of macromolecule is regulated by the changes in local solution conditions, another exotic phenomenon appears and that is the attraction at isoelectric point, known as Kirkwood-Shumaker interaction (KS) [3]. KS interaction obeys different scaling law than van der Waals interaction, ubiquitous between electroneutral bodies. Here we present a theory that brings these two exotic phenomena together. Namely, we studied a model system with dissociable sites uniformly distributed across two plane-parallel surfaces in a mixture of monovalent and polyvalent salt. We generalized existing field-theoretic approach to properly include charge regulation phenomenon in its formalism [4] and derived the general form of Kirkwood-Shumaker interaction, valid also in regime where their original result fails [5].

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# Rheology of nano-confined ionic liquids between metallic surfaces

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Many new emerging applications of Ionic Liquids involve their properties at conducting solid surfaces and/or under electric fields [1]. These include energy-related applications such as super-capacitors, batteries, electro-actuators in which IL are used as electrolytes. In these devices the dynamical and rheological properties of IL's under confinement are a key element for energy conversion efficiency and power density. But peculiar dynamical properties of IL's at metallic surfaces or under electric field have been reported [2], that are presently discussed in relation to structural phase transitions at metallic electrodes, [3,4] and/or capillary-freezing under confinement [5] associated to charge-image effects.

We report investigations of the flow properties of BmimPF<sub>6</sub> confined between metallic surfaces (platinum) and dielectric surfaces (borosilicate) with a Surface Force Apparatus (SFA) using a squeeze flow. Our apparatus features 4 orders of magnitude for confinement values from 1nm to 10 $\mu$ m, allowing one to bridge microscopic to macroscopic rheological properties, as well as an extended frequency range up to 300 Hz. We find that between dielectric surfaces and for confinement larger than 10 molecular size, the IL behaves as a purely Newtonian liquid with a no-slip boundary condition located on the borosilicate surfaces. However on Platinum surfaces, the position of the no-slip plane depends on the confinement and reveals the presence of a complex surface structure with a thick frozen pre-wetting layer.

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# Equilibrium Studies on the Separation of Acetic Acid from Aqueous Solutions by Bulk Ionic Liquid Membrane Containing Tributyl Phosphate

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Acetic acid is widely used in variety chemical industries such as food, pharmaceutical, dyeing and printing. Acetic acid is often found in wastewaters of these chemical industries and has been produced in aqueous streams as a by-product of the fermentation processes [1,2].

Ionic liquids are salts composed of certain anions and cations that are liquid around the room temperature. They are also as an alternative to classical organic solvents and they are called “green solvents”. The vapor pressure of ionic liquids is very low and they are even stable at high temperature. Ionic liquids have increased interest in different separation applications due to their important properties [3,4].

Recently, bulk liquid membranes have gained importance due to its transport efficiency, high selectivity, simple handling and low capital and operation costs. Bulk liquid membrane (BLM) which is a type of liquid membranes consists of feed and stripping phase contact with a membrane phase [5,6]. The membrane phase has the ability of selective transport of mixture components. When ionic liquids are used in the membrane phase are called bulk ionic liquid membrane (BILM) [7].

In this study, the separation of acetic acid from aqueous solutions through bulk ionic liquid membranes was investigated. Tributyl phosphate (TBP), dissolved in ionic liquid (1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIM][Tf<sub>2</sub>N])), was used as an extractant in the membrane phase. In the experiments, 5% (w/w) and 10% (w/w) acetic acid solutions were used as feed phase, different concentration of NaOH solutions within the range of 0-4 N were used as stripping phase, and different concentration within the range of 0-2 mol/l TBP dissolved in [BMIM][Tf<sub>2</sub>N], were used as membrane phase. The distribution coefficient and extraction efficiency of these bulk ionic liquid membrane systems were calculated, and compared. The separation study shows that BILM was used as effective technique for the separation of acetic acid from its aqueous solutions.

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## Removal of Acetic Acid from Water by using Tributyl Phosphate Dissolved in Ionic Liquid [BMIM][Tf<sub>2</sub>N]

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Acetic acid is most widely used in many industrial processes such as food, pharmaceutical, printing and dyeing. Acetic acid has been widely produced in aqueous solutions by fermentation processes. Reactive extraction of acetic acid provides an effective removal from water including lower than 10% (w/w) acid concentrations [1,2].

Ionic liquids are a new group of solvents that are composed of certain anions and cations. They have important properties such as high thermal stability and very low vapour pressure that make them attractive for various removal and separation applications and they are also called “green solvents” [3,4].

In this study, reactive extraction of acetic acid from water using tri-n-butyl phosphate (TBP) dissolved in ionic liquid [BMIM][Tf<sub>2</sub>N] has been examined. TBP were used as an extractant. The effect of the different initial acetic acid concentrations (5-10% (w/w)) and phase volume ratio (feed phase volume/organic phase volume) (0.5-1.5) on the removal efficiency were investigated. The experimental results were evaluated by means of the distribution coefficient (D), loading factor (Z), and extraction efficiency (E). This reactive extraction study by using TBP dissolved in ionic liquid [BMIM][Tf<sub>2</sub>N] showed that it was an efficient removal process for the recovery of acetic acid from water.

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# Electrochemical behavior of uranyl ions in ionic liquid, 1-butyl-3-methylimidazolium chloride

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Ionic liquids have attracted significant attention in the field of nuclear fuel cycle because they have several attractive properties such as an amazing ability to dissolve organic and inorganic compounds, and a wide electrochemical window suitable for aqueous and non-aqueous reprocessing applications. Ionic liquids are being evaluated as an alternative to the conventional diluent, n-dodecane, in aqueous reprocessing, and as a substitute to the traditional high-temperature molten salts in the non-aqueous reprocessing of spent nuclear fuels [1, 2]. In this work, as a part of the research to recover uranium from spent nuclear fuel using ionic liquid, the electrolytic reduction of uranyl nitrate in ionic liquid, 1-butyl-3-methylimidazolium chloride (bmimCl), was studied. The electrochemical behavior of uranium(VI) in bmimCl was investigated within the temperature range of 343–373 K through cyclic voltammetry (CV).

All electrochemical experiments were carried out in a three-electrode cell. For cyclic voltammetric measurements, a glassy carbon (cylindrical, SA = 0.07 cm<sup>2</sup>) and a Pt wire were used as a working electrode and a counter electrode, respectively. As a quasi-reference electrode, a Pt wire was used.

The ionic liquid, bmimCl, exhibits an electrochemical window of 2.7 V with a cathodic stability of up to -1.4 V (vs. Pt), which is sufficient for enabling the reduction of uranyl ions. The cyclic voltammogram of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in bmimCl consists of a reduction wave occurring at the peak potential of -1.05 V owing to the reduction of U(VI) and an oxidation wave occurring at the peak potential of -0.90 V. The result from the CV experiments at various scan rates and temperatures indicates that a reduction of uranyl ions takes place through a quasi-reversible single-step two-electron transfer reaction. The diffusion coefficient of U(VI) in bmimCl was estimated to be on the order of 10<sup>-8</sup> cm<sup>2</sup>/s.

Electrodeposition experiments were conducted at different potentials ranging from -0.8 V to -1.5 V on a glassy carbon plate cathode. In the potentiostatic electrolysis of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in bmimCl, black and dense particles were deposited on the surface of the electrode. The Faradaic efficiency of the electrodeposition was 40%–55%. An EDS analysis of the deposit indicated that the product was uranium oxide, and the atomic ratio of O to U was about 2. An XRD pattern of the as-deposited material showed that it was amorphous, and no XRD signal was obtained. However, a distinct XRD pattern of UO<sub>2</sub> evolved by heating the deposit to 1,073 K under an inert atmosphere for one hour. The results therefore indicate that uranyl nitrate is reduced to UO<sub>2</sub> in an ionic liquid medium. However, a reduction to a metallic form was not observed under the present conditions, and further investigation is now under way.

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## Phase behaviors of ionic liquids and ionic liquid crystals

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Ionic liquids (ILs) are salts composed of large ions whose melting points are around room temperature. They are typical complex liquids attributed to the subtle balance and competition between their microscopic molecular interactions, such as electrostatic, van der Waals, hydrogen bonding, and chemical bonding interactions, whose physical properties can hardly be described by simple liquid theories. Moreover, in recent years, ionic liquid crystals (ILCs), the liquid crystal phases formed by ionic liquids, have also been attracting more and more attentions. By utilizing multiscale molecular dynamics simulations, we have been investigating various phases of ILs/ILCs for more than 10 years, and discovered their following phase behaviors: (1) ILs with intermediate alkyl side chains form nanoscale heterogeneous structures (NHS) with a continuous polar network composed of charged anions and cationic head groups as well as separated nonpolar domains composed of cationic side chains [1]; (2) when varying the strength of an externally applied electric field, ILs go through multiple phase transitions [2, 3]; (3) by tuning the temperature, the alkyl cationic side-chain length, and the strength of electrostatic interactions, ILs change among different phases including simple liquids, NHS, and ILCs [4, 5]; (4) the anomalous dynamic property of ILs that larger cations diffuse much faster than smaller anions can be qualitatively explained by the recently developed SCGLE theory [6], indicating that ILs at room temperature can reside in a partially arrested glassy state. Along with other on-going simulation works in our group on phase transitions induced by various thermodynamic conditions, those simulation results beckon the development of a unified analytical model describing all phase behaviors of ionic liquids as complex liquids from the viewpoint of subtle balance and competition between microscopic molecular interactions in ILs/ILCs.

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# A Simple Method for Efficient Synthesis of Tetraarylporphyrin using Acidic Ionic Liquids

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Ionic liquids (ILs) could be suitable and environmentally safer replacements for the volatile, toxic, and flammable organic solvents. In fact, there are various reports about using ILs as reaction media and catalysis. We have studied the utilization of acidic ILs to prepare TPPs.[1,2] This method could reduce the halogenated reaction medium to 1/15 amount and could be reused ten times without any loss in catalytic activity. Recently we also reported the TPP preparation in acidic ILs using Adler method. [3,4] The Adler method is more green than the Lindsey method in terms of no use of harmful halogenated solvents, acid catalysts such as  $\text{BF}_3$  and oxidant such as DDQ. Furthermore, the use of acidic ILs instead of propionic acid makes possible a more green porphyrin synthesis. In fact, the TPP was obtained in 15% yield in  $[\text{HC}_4\text{im}][\text{CF}_3\text{CO}_2]$ , which was similar to the yield obtained in propionic acid (15%). In addition,  $[\text{HC}_4\text{im}][\text{CF}_3\text{CO}_2]$  could be reused at least 3 times without any loss in its catalytic activity. The use of the acidic ILs for porphyrins synthesis can afford the porphyrins without producing any acid waste. In the various acidic ILs, only the imidazolium type ILs,  $[\text{HC}_4\text{im}][\text{X}]$ , could provide TPP. Herein we report the optimum acidic ILs for the porphyrin (TPP and TPyP) preparation with focus on their anion structures, and the simple and efficient green method for the synthesis of TPyP using the acidic ILs as the acid catalytic media instead of the propionic acid which is troublesome to remove from the reaction mixture.

We investigated the tetraphenylporphyrin (TPP) preparation using the several acidic ionic liquids,  $[\text{HC}_4\text{im}][\text{X}]$  ( $\text{X}^- = \text{CF}_3\text{SO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{CF}_3\text{CO}_2^-$ ,  $\text{BF}_4^-$ ), as acid catalytic media. For such the acidic ionic liquids, the anion ( $\text{X}^-$ ) of  $[\text{HC}_4\text{im}][\text{X}]$  is related to the acidity of ionic liquids, and affect the porphyrin formations. This synthetic method using acidic ionic liquids can also be applied to other *meso*-substituted phenyl porphyrins and 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine, TPyP which has 4-pyridyl moieties at four *meso* positions. In  $[\text{HC}_4\text{im}][\text{CF}_3\text{CO}_2]$ , the TPyP could be obtained in 11% yield, and  $[\text{HC}_4\text{im}][\text{CF}_3\text{CO}_2]$  could be reused at least 3 times without any loss of its catalytic activity. The TPyP synthesis methodology using the acidic ionic liquids can remove the acidic ionic liquids from TPyP only by easy filtration in contrast to traditional Alder method which need vacuum distillation or liquid-liquid extraction for removing propionic acid. Our proposed porphyrin preparation methods using the acidic ionic liquids potentially have wide applications to various useful porphyrin analog.

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Ionic Liquids (ILs) become object of interest in many areas such as electrochemistry, photochemistry, environmental engineering etc. It's mainly caused by great number of possible anion-cation combination, thus we can find combination that would have desired properties. However, performing only on the experimental research to find the optimal combination is impossible. For that reason using computational tools for estimating properties that could be significant for our goal become necessary.

In this study we have developed a Quantitative Structure–Property Relationship (QSPR) model that allows predicting the logarithmic values of the dielectric constant ( $\epsilon$ ) - one of the key parameters that represents the polarity and solvating capability of ionic liquids. This mathematical model correlates the structure of ionic liquid with the value of dielectric constant. Based on developed model equation we estimated values of  $\log \epsilon$  for 1 000 ILs, for which the experimentally measured values had been unavailable.

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# Effect of Anionic Structure of Ionic Liquids on Thermal Cyclization of Chromene Derivatives with Polar Substituents

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Unlike molecular solvents consist of one single component, ionic liquids are composed of anion and its counter ion. In order to use ionic liquids as media appropriately, it is important to consider the ion–solute interaction, namely the solvation behaviour. The size of ions constituting ionic liquids are relatively larger, and there is an ionic interaction between a cation and an anion. For these features, ionic liquids have higher viscosity than ordinal molecular solvents. Asano et al. demonstrated the thermal isomerization of molecules in their electronic ground state are retarded with an increase in pressure by combining high pressure and visous molecular solvents [1]. Recently, we also observed the pressure-induced retardations, so-called dynamic solvent effect in ionic liquids which are resulted from the slow thermal fluctuations of ions by high viscosities [2]. The structure of ionic liquids affects not only viscosity but also other physical properties such as polarity and hydrophilicity. These properties effect on the solvation behaviour of ionic liquids. Herein, we studied the influence of the anionic structure of ionic liquids and the influence of substituent structure of solute such as polarity and electronic properties on the dynamic solvent effect.

We selected the thermal cyclization of a coloured chromene **1**, 1-(3,3-diphenylprop-2-enylidene)naphthalen-2-one, derivetives as a probe reaction in ionic liquids. The chromene **1** was photochemically generated in situ from 3,3-diphenyl-3*H*-naphto[2,1-*b*]pyran derivatives **2**, and its decay was followed spectrophotometrically. We also introduced to the methoxy, cyano, and methyl substituents on the para position of 3,3-diphenyl groups in **1** and measured the pressure effects on the thermal ring closure rate of reaction in ionic liquids.

The reaction was retarded with increasing pressure in highly viscous ionic liquids such as [bmim][Sac] and [bmim][CS]. The reaction rate in [bmim][CS] was decelerated considerably because of its high viscosity. In case of [bmim][Sac], the increasing pressure exerts an effect on the formation of the  $\pi$ – $\pi$  stacking interaction between chromene derivatives and Sac anion, and the chromene derivatives are solvated by [bmim][Sac] efficiently. Thus, it seems to surmise that the retardation of the reaction was observed. In the effect of the substituent structure of the chromene derivatives, the reaction rates were greatly retarded with increasing pressure in case of using the chromene derivatives with polar substituents as compared to the chromene derivatives with non-polar substituents. It is reasonable to surmise that the chromene derivatives with polar substituents can be strongly solvated with the ionic liquids, and the retardation of the reaction was observed.

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## Topology of liquid aluminium

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Using *ab initio* Molecular Dynamics (AIMD) and implementing a thermal process developed in [1] (Modified San Diego thermal process), we generated three liquid aluminum supercells at 947 K, 1023 K and 1323 K. In order to study their structural properties we simulated the final atomic topology of the liquid by averaging several energy-equivalent structures generated at the end of the MD process. To characterize them and obtain the short range ordering we calculated the Pair Distribution Function (PDF) of each liquid supercell as well as the Flat Angle Distribution (FAD). We also obtained the coordination number of liquid aluminum for the above-mentioned temperatures.

Our results show that in the liquid phase the dominant short range order is of the icosahedral type and this varies depending on the temperature of the liquid. A discussion will be presented to compare our results with the Frank-Kasper polyhedral structures studied several decades ago and found recently in several studies of liquid metals.

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## Shear Viscosity of liquid alloys

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The shear viscosity of liquid K-Cs and Li-Bi is studied by molecular dynamics simulations using Green-Kubo relation. Interatomic interactions are described by pair potentials obtained from Fiolhais pseudopotential for the first one, and a multiscale approach for the second one.

Simulation results are compared with available experimental data. The influence of composition and temperature is examined.

While K-Cs is a rather random mixture, Li-Bi is strongly hetero-coordinated and the influence of chemical order is highlighted.

# Phase behaviour of primitive models of ionic fluids confined in disordered matrices: collective variables approach

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Over the past several decades, the phase diagrams and the critical behaviour of ionic fluids with dominant Coulomb interactions have been intensively studied by using experimental and theoretical methods. A major part of theoretical and numerical works have been focused on the phase diagram of the primitive model (PM) consisting of an electroneutral mixture of charged hard spheres immersed in a structureless dielectric continuum. Considerable efforts have been made in order to develop theories for the description of vapour-liquid phase behaviour in these systems. A number of important results have been obtained by using the theory that exploits the collective variables (CVs) method [1]. In contrast to the bulk case, the phase behaviour of ionic fluids in disordered confinements has not been studied well.

In the present work, we report the recent progress in the development of CVs based theory to study the vapour-liquid equilibrium of PMs confined in a disordered porous matrix. Considering the matrix-fluid system as a partly-quenched model, we combine the method of CVs with the scaled-particle theory (SPT) recently proposed for a multi-component hard-sphere fluid confined in disordered hard-sphere matrices [2]. This approach allows us to formulate the perturbation theory using both the SPT and the CVs method and to describe the thermodynamics of a reference system. Following the ideas proposed for the bulk PM [1], we derive an explicit expression for the relevant chemical potential of the confined ionic system which takes into account the third-order correlations between ions. Based on this expression, the phase diagrams for the PM fluid are built at different matrix porosities as well as for the different sizes of matrix and fluid particles. It is observed that coexististance region gets narrower with a decrease of the matrix porosity, and simultaneously the critical temperature ( $T_c$ ) and critical density ( $\rho_c$ ) become lower. On the other hand, an increase of size of matrix particles at the fixed porosity increases the critical parameters  $T_c$  and  $\rho_c$ , while the assymetry in size of positively and negatively charged ions essentially strengthens the tendency of  $T_c$  and  $\rho_c$  towards lower values.

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# Molecular dynamics investigation of a coarse-grained model of ionic liquid under confinement and shear

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In the current work we present an approach for simulating mesoscopic phenomena related to lubrication with ionic liquids [1]. We have implemented a coarse grain molecular dynamics (MD) [2] description of an ionic liquid as a lubricant which can expand into lateral reservoirs. Ionic liquid (IL) consists of an equal number of cations and anions, represented as coarse-grained particles charged with elementary charge, which are placed between fcc (111) plates (referred to as the top and bottom plate). Interactions in our system include non-bonded Lennard-Jones and Coulombic potentials. Our geometry allows a variable confinement gap (plate-to-plate distance) and a variable amount of lubricant in the gap, while avoiding the squeeze-out of the lubricant into vacuum. Ions are initially randomly placed inside the confinement gap and they are equilibrated.

We observe that IL confined between surfaces features alternating positive and negative ionic layers, with an interlayer separation corresponding to the ion pair size. We observe nonmonotonic dependence of the normal force (acting on the top plate) on plate-to-plate distance. At small plate-to-plate distances we observe a steep rise of that normal force. This is an interesting behaviour that could potentially be exploited for preventing solid–solid contact and wear. The shear simulation results have revealed two distinct regimes of lubrication: elasto-hydrodynamic regime of lubrication, under low loads and lubrication regime with low and velocity-independent specific friction, under high loads.

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## Thermodynamic and structural properties of 2D ionic liquids and charge ordering

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The structural properties of model two-dimensional ionic liquids are examined, with a particular focus on the charge ordering process. Computer simulation and integral equation theories are used. The influence of the Coulomb form of the interaction, versus that of a screened interaction, is analysed, particularly with respect of reproducing the charge ordering property. The influence of charge ordering in the low density regime is discussed in relation to well known properties of 2D Coulomb fluids, such as the Kosterlitz-Thouless transition and criticality. The study points to the existence of a stable thermodynamic cluster phase, indicating the existence of a liquid-liquid phase transition. The liquid-gas and Kosterlitz-Thouless transitions would then take place inside the predicted cluster phase.

# Electrochemical four-electron reduction of dioxygen by diiron complex promoted in an ionic liquid-modified electrode

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A non-heme diiron(II) complex (**Fe<sub>2</sub>**), which was prepared as a model of the active centers of hemerythrin and methane monooxygenase that have dioxygen-carrying and dioxygen-activating functions, respectively, was prepared, which was supported in an phosphonium-/ammonium-type ionic liquid-modified Au electrode (**Fe<sub>2</sub>@1/Au**) [1]. The diiron complex **Fe<sub>2</sub>** is stabilized by entrapment inside the ionic liquid layer, which exhibited an electrochemical behavior similar to that in homogeneous solution, as well as catalytic O<sub>2</sub> reduction activity in aqueous solution at ambient temperature. Rotating ring disk electrode measurements demonstrated a catalytic current at 0 V vs. Ag/AgCl, which is indicative of four-electron reduction of O<sub>2</sub>. Next, we prepared the ammonium-type ionic liquids with three terminal olefins and polymerized to encapsulate the complex on the electrode surface by an olefin metathesis reaction (**Fe<sub>2</sub>@poly-1/Au**). Interestingly, the catalytic four-electron reduction of O<sub>2</sub> is enhanced after encapsulation of the diiron(II) complex, **Fe<sub>2</sub>**, by polymerization of the ionic liquid on the surface. The apparent number of electrons ( $n_{app}$ ) related to the O<sub>2</sub> reduction process before encapsulation was estimated to be only 3.2 [2]. However,  $n_{app}$  was significantly improved to 3.8 after the encapsulation [3].

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# Intrinsic Structure of the Interface of Partially Miscible Fluids: An Application to Ionic Liquids

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In this contribution, we will show result from Molecular Dynamics simulations on how the intrinsic surface structure of liquid/liquid interfaces involving ionic liquids (ILs) depends on the opposite phase of varying polarity. We study 1-n-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF<sub>6</sub>) and 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM NTf<sub>2</sub>). The opposite phase is either cyclohexane, benzene, or water, but as a reference, IL–vacuum interfaces are also studied. We combine a distance-based cluster search algorithm with the ITIM intrinsic analyzing method to separate liquid phases showing non-negligible mutual miscibility and to identify atoms residing at the instantaneous surface. In contrast to the well structured surface of IL–vacuum systems, at liquid/liquid interfaces of ILs density correlations, ionic associations, and orientational preferences are all weakened, this effect being much more pronounced when the other species is water. In such systems we observe a drastic reduction in the presence of the cation at the surface and an increase of appearance of polar moieties (of both the cations and anions) leading to decreased apolar character of the interface. Furthermore, cations are mostly found to turn with their butyl chains toward the bulk while having their methyl groups sticking toward water. Anion–cation associations are reduced and partially replaced by water–anion and rarely also water–cation associations.



## Efficient 3d Ewald summation method for simulating inhomogeneous charged systems with slab geometry

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We present a new approach to efficiently simulate electrolytes confined between infinite charged walls using a 3d Ewald summation method. The optimal performance is achieved by separating the electrostatic potential produced by the charged walls from the electrostatic potential of electrolyte. The electric field produced by the 3d periodic images of the walls is constant inside the simulation cell, with the field produced by the transverse images of the charged plates canceling out. The *non-neutral* confined electrolyte in an external potential can be simulated using 3d Ewald summation with a suitable renormalization of the electrostatic energy, to remove a divergence, and a correction that accounts for the conditional convergence of the resulting lattice sum [1, 2].

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## Transverse excitations in a van der Waals-like liquid Hg

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Transverse acoustic (TA) phonon modes usually cannot be detected in liquids by ultrasonic or optical measurement because the shear force in the long spatial range is very weak. When the vibration wavelength in a liquid approaches the atomic nearest neighbor distance, however, there may be a solid-like cage effect on the nanometer scale that acts as a restoring force for TA modes. In the previous inelastic x-ray scattering (IXS) experiment,  $S(Q, \omega)$  spectra of liquid Ga [1], Sn [2], Fe [3], Cu [3], and Zn [3] were measured at BL35XU of SPring-8 [4] near the melting points, and low-energy excitations were observed between the quasielastic line and the longitudinal acoustic (LA) mode. From the detailed analysis for the IXS data, the lifetime of sub-*ps* and the propagating length of sub-*nm* were estimated from the TA phonon modes in each liquid metal measured, which may correspond to the lifetime and size of cages formed instantaneously in liquid metals. Short-lived covalent bondings are contributed in liquid Ga, Sn, and Zn, whereas icosahedral clusters do exist in liquid Fe and Cu.

In this study, we examine the existence of the TA mode in one of the simplest liquid metals, liquid Hg, by measuring IXS at BL35XU/SPring-8 [4] at room temperature. The LA modes are clearly seen in the measured IXS spectra as shoulders, in good agreement with the previous IXS data [5]. A very interesting feature in the spectra is that in the low energy region between the LA modes and the quasiclastic peak, the gaps are buried or even have shoulders. From the analysis of the current correlation functions,  $C(Q, \omega) = (\omega/Q)^2 S(Q, \omega)$ , the LA excitations were clearly observed, and the excitation energies highly exceed the hydrodynamic prediction by about 40%, much greater than those in other liquid metals and similar to those of molecular liquids with van der Waals intermolecular correlations. The TA excitation modes can be detected through the quasi-TA branches in the longitudinal spectra. The microscopic Poisson's ratio was obtained from the excitation energies of the TA and LA excitation modes to be  $0.40 \pm 0.02$ , which is a very soft value like a rubber and indicates no well-defined rigid clusters in liquid Hg.

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This presentation reflects on the well-known quasiuniversality of simple liquids' structure and dynamics [1, 2, 3, 4, 5]. We discuss two possible justifications of it [6, 7]. The traditional one is based on the van der Waals picture of liquids in which the hard-sphere system reflects the basic physics. This paper presents an alternative explanation, which argues that all quasiuniversal liquids to a good approximation conform to the same equation of motion. This explanation uses the exponentially repulsive pair-potential system as the fundamental reference system, which in contrast to the hard-sphere system is analytical.

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# The influence of electronic polarizability on the properties of ionic liquids

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In recent years, ionic liquids gained a lot of relevance in technological applications, such as supercapacitors, where the ionic liquids are usually under strong confinement. It has been shown that the inclusion of electronic polarization effects is necessary to properly describe ionic liquids, in particular to correctly reproduce their dynamical properties in molecular dynamics simulations.

To this aim, we developed a coarse-grained polarizable force field for the ionic liquid BMIm/PF6 based on a pre-existing non-polarizable model [1]. These geometrically identical, yet intrinsically different models allow us to investigate the influence of electronic polarization effects with respect to structural and dynamical properties of ionic liquids in solution, at interfaces, and in confined geometries, revealing their importance in molecular modeling.

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# **Topic 2**

## **Water, Solutions**

# Common microscopic structural origin for water's thermodynamic and dynamic anomalies

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Water displays a vast array of unique properties, known as water's anomalies, whose origin remains subject to debate[1-5]. With computer simulations of popular water models, we provide here a unified picture of water's anomalies in terms of locally favoured structures, which are 'microscopically' identified by the high tetrahedral and translational symmetries stabilized by four hydrogen bonds. We reveal that such local structural order has different impacts on the thermodynamic and dynamic properties of water: The former is controlled directly by the structural order parameter itself, whereas the latter is by the one coarse-grained up to nearest neighbours, reflecting the fact that the dynamics of a molecule is determined under an influence of its nearest-neighbour environment. We show that these two structural order parameters intimately linked only via spatial coarsegraining, quantitatively account for thermodynamic and dynamic anomalies respectively. By a two-state scenario, water's thermodynamic anomalies as well as dynamical anomalies including diffusion maximum under compression, dynamic slowing down upon cooling, "strong-to-fragile" transition, dynamic heterogeneity, and breakdown of the Stokes-Einstein-Debye relation are all explained in a coherent manner. We argue that it is this two-state feature that is the origin of water's anomalies and allows water to change its physical and chemical properties so flexibly

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## Characterization of dynamic crossovers in bulk liquid water by molecular dynamics simulations

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Dynamic cross-overs in bulk water are important for the study of glass-forming liquids and implicated in many phenomena of biological interest. Here we use classical molecular dynamics (MD) simulations to characterize the interplay between dynamic crossovers and microscopic behaviour of bulk liquid water in the temperature range 180 – 350 K.

In particular, we focused to the dynamic crossover, which is involved in favouring the unfolding of proteins, found experimentally at  $T^* \sim 315 \pm 5$  K [1,2]. Computationally, a cross-over from Vogel-Fulcher-Tamman to linear trend for increasing temperature was detected from the Arrhenius plots of dynamic quantities, namely of the inverse diffusion coefficient and of the rotational constant and from the onset of a further heterogeneity in the rotational relaxation [4], but we propose some other possible statistical tools. We also verified that for the coefficient of thermal expansion  $\alpha_P(T,P)$  the isobaric  $\alpha_P(T)$  curves cross at about the same  $T^*$  as in the experiment.

We used two different potential models for water: TIP4P-Ew and a recently proposed model (OPC) [3]. OPC was developed by Onufriev *et al.* through the optimization of the distribution of point charges to best describe the “electrostatics” of the water molecule, which reproduces a comprehensive set of bulk properties significantly more accurately than commonly used rigid models.

Simulations predict  $T^* \sim 285 \pm 5$  K for the TIP4P-Ew models, but  $T^* \sim 309 \pm 5$  K for the OPC model. The lifetimes of water hydrogen bonds and of the nearest neighbours were evaluated and were found to cross near  $T^*$ , where the lifetimes are about 1 ps. For  $T < T^*$ , hydrogen bonds persist longer than nearest neighbours, suggesting for  $T < T^*$  a prevalence of the hydrogen bonding network in water structure, while for  $T > T^*$  water behaves more like a simple liquid. The fact that  $T^*$  falls within the biologically relevant temperature range is a strong motivation for further analysis of the phenomenon and its possible consequences for biomolecular systems.

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## COSMO-RS: The currently most tool for the prediction of free energies of molecules in solution

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Since its first publication in 1995 the COSMO-RS method [1,2,3] has been developed to one of the most efficient and most accurate computational methods for the predictive evaluation of fluid phase thermodynamics, i.e. the free energies of molecules in the liquid phase. Indeed, the results of recent benchmarks [4,5] and blind challenges [6] proof that it seems to have only half of the error bars of force-field based simulations, despite of requiring only a small percentage of the respective computational resources.

Apart from many chemical engineering applications it is nowadays routinely used in various areas of chemistry, cosmetics and pharmaceutical chemistry for solvent, co-solvent or anti-solvent screening and even for co-crystal screening. In this talk a short survey of the COSMO-RS method will be given, together with some representative applications and accuracy statistics.

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## Ultrafast energy fluxes during solvation dynamics in liquid water

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We and several colleagues previously developed a work and power analysis scheme to unravel the ultrafast energy fluxes resulting from excitation of solute vibrations or rotations in neat liquid water. This revealed the identity and sequence of solvent modes/hydration shells absorbing the excess energy, and provided a qualitative and quantitative picture of the energy transfer pathway. More recently, we have applied the same energy flux approach to bring a previously absent molecular level perspective to the much-studied 'solvation dynamics' problem [1,2,3]. We focus on the classic, neutral monatomic solute immersed in water solvent, subjected to a sudden acquisition of a unit charge, here in a nonequilibrium perspective. The path and time scales of the subsequent energy flow to the water solvent's translations, rotations, and vibrations are analyzed via the energy flux scheme, as are the contributions from different hydration shells, and rotational axes. Other central issues, related to linear response theory, 'inverted' snowball effects, and inertial relaxation, are also analyzed.

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## Ion-specific effects in aqueous polyelectrolyte solutions - volumetric and calorimetric properties of ionene salts

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While the ion-specific effects in aqueous solutions of simple electrolytes are a subject of numerous extensive studies, much less is known about the ion-specific effects in polyelectrolyte solutions. The physical and chemical properties of these systems strongly depend on the linear charge density of the polyion (or its hydrophobicity), as well as on the chemical nature of the counterions (ion specific effects) [1]. To understand the mutual influence of the polyion charge density and the nature of the counterions on the thermodynamic and transport properties of these materials, several studies of thermodynamic [2-4] and dynamic [5-7] properties of aqueous ionene solutions have been performed in the past. It's been established that the observed ion-specific effects can be understood as a consequence of relative strength of ion-ion, ion-water, and water-water interactions.

Here we focus on the role of the structure of the hydration water on the ion-specific effects, as reflected in the volumetric (partial and apparent molar volumes) and calorimetric properties (apparent heat capacities). Aqueous ionene solutions were studied using the oscillating tube densitometer and differential scanning calorimeter. The polyion's charge density and the counterion properties were systematically varied. The special attention was put into evaluating the electrostatic and hydrophobic contribution to the properties studied [8].

The results show that both polyions and counterions are contributing to the structuring of the hydration water, reflecting the importance of the fraction of condensed counterions. Although dominating, the electrostatic contribution alone is not sufficient to explain the hydration of polyelectrolytes studied; the thermodynamic data suggest that the CH<sub>2</sub> groups that are not in the direct vicinity of the charged groups in the polyion backbone, structure the surrounding water hydrophobically. Synergistic effect between polyion and counterions was observed.

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## Droplet-like nanoscale heterogeneity in aqueous solutions of polar organic compounds

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A droplet formation in aqueous solutions of some polar organic solutes, such as tetrahydrofuran and tert-butanol, has been experimentally detected at the submicrometer scale using two independent laser diagnostic techniques (dynamic light scattering and laser phase microscopy) and described in terms of water-solute intermolecular hydrogen bonding. It is shown that the nanodroplets have a size on the order of 100 nm, their refractive index is higher than that of the ambient liquid, and they are highly enriched with solute molecules. The maximum of light scattering intensity falls within the solute concentration range 2–10 mol.%, which corresponds to the volume number density of the nanodroplets  $\sim 10^{10}$ – $10^{11}$  cm<sup>-3</sup>.

A theoretical explanation for the formation of nanodroplets with a high content of the solute is proposed in terms of “twinkling” hydrogen bonds, whose dynamics is described by the model of dichotomous noise [1]. The results of theoretical calculations, carried out within this model, show that at low concentrations of the solute, the system must be with high probability in the unstable region, confined to the so-called “dichotomous” spinodal. The nanodroplet formation can be considered as a specific self-assembly, resulting from the process of the spinodal decay. This implies that the system is affected by a single-frequency long-wave excitation (the so-termed single-frequency phonon) at every moment of time, and some spatial areas at the nanometer scale (mesoscopic areas) produce a coherent response to the action of such phonon, so that the intermolecular hydrogen bonds behave self-consistently within these areas. We assume that the nanometer-sized droplets of pure solute in aqueous solutions are just such coherent areas. The phase diagram for the binary system “water – polar solute” is first constructed with taking into account cross-link hydrogen bonds.

The proposed theoretical model expands the traditional concepts of physical chemistry, such as infinite solubility. First of all, it concerns the polar molecules, which are considered infinitely soluble in water.

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# Experimental investigation of critical Casimir forces in binary liquid mixture by blinking optical tweezers

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Casimir forces arise because of the quantum vacuum fluctuations of the electromagnetic field when confined between two conducting surfaces. Analogously, critical Casimir forces are due to the thermal fluctuations of the concentration in a binary liquid mixture near its critical demixing point when spatially confined between two surfaces [1-3]. The range of critical Casimir forces is strongly temperature-dependent because it is set by bulk correlation length of the binary mixture, which diverges upon approaching the critical temperature  $T_c$  [4].

We consider two polystyrene beads immersed in a water-lutidine solution near its critical point. These particles are subject to an optical and electrostatic potential as well as to critical Casimir forces when the temperature of the mixture approaches  $T_c$ . We could observe that at sufficiently small distances, the concentration fluctuations of the solvent are confined by the surfaces of the particles, modifying their interaction. Because the optical potential can screen or otherwise affect the critical Casimir forces on the particles, we used blinking optical tweezers to investigate the interaction between the particles when they are not subject to the confining optical potential [5].

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## Characterization of water confined into nanoscale hydrophobic pores

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The molecular structure of water and ice are important from a structural and mechanistic perspective for a broad range of applications. Particular interest has received a behavior of water close to the hydrophobic surfaces, which drives many important phenomena such as folding of proteins and the formation of micelles and membranes.

The question, how the interactions with confining surfaces changes the water structure, dynamics, and thermodynamics properties, remains however open. To gain a deeper understanding in the involved mechanisms we have studied the water confined into hydrophobic porous carbon CMK-3 and CMK-8 and hydrophobic zeolite Al (PO<sub>4</sub>)<sub>5</sub> with pores size ranging from 6 to about 1 nm respectively. For characterization of structure and dynamics of confined water and ice we have used neutron powder diffraction and spectroscopy in a broad temperature range from 1.5 K to 300 K. Variation of humidity provided an additional insight into the formation of the hydrogen bonds and the cooperative interactions between water molecules and confined matrix.

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## New Potential Model for Propylene Glycol: Insight to Local Structure and Dynamics

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Propylene Glycol (1,2-propanediol) is a viscous liquid with a low freezing point (around 213 K). It is a popular solvent, which use covers several industrial areas, such as pharmaceutical, cosmetics and food. Its ability for decrease the freezing point of water together with a low toxicity enables its use in antifreezing solutions and cryopreservation of tissues [1-3]. Studying the microscopic organization and dynamics of the individual solvent is an important and necessary first step towards understanding and predict the properties of propylene glycol-based solutions.

The goal of the present work is to develop a new potential (force field) for propylene glycol, based on the transferable OPLS all-atom potential model. Ab initio calculations were carried out to gather the atomic charges and dihedral angle parameters. For oxygen atoms of the hydroxyl groups, the van der Waals radius ( $\sigma$ ) were changed in a heuristic manner.

The potential was carefully validated against various experimental properties, such as density, self-diffusion and viscosity, among others, in a wide temperature range (from 273.15 up to 373.15 K). The structural properties of propylene glycol at a molecular level are discussed in terms of atom-atom, center-of-mass radial distribution functions and hydrogen bonds.

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# Viscosity of supercooled water under pressure and two-state interpretation of water anomalies

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Among the numerous anomalies of water, the effect of pressure on its transport coefficients is particularly striking. Around room temperature, an increase in pressure from ambient results in a decrease of viscosity and rotational correlation time, while the translational diffusion coefficient increases. At high enough pressure, around 200 MPa, the pressure dependence is reversed and water behaves as a normal liquid. The pressure anomalies for translational and rotational diffusion have been followed deep in the supercooled region. However, up to now, viscosity data for supercooled water under pressure was not available. We report for the first time such data, obtained with a Poiseuille flow experiment performed up to 300 MPa and down to 20°C below the melting line. Our data reveal a large intensification of the viscosity anomaly upon cooling: pressurization at 244 K reduces the viscosity of water by nearly a factor of 2. The location of the viscosity minimum follows that of the translational diffusion coefficient maximum.

We discuss experimental data on dynamic properties in the framework of two-state models for water. Combining a modified version of a previous dynamic model [1] with an existing, quantitative model for thermodynamics [2], we obtain an accurate description of dynamic properties of stable and supercooled water under pressure. We discuss the possible connection with a putative phase transition between two distinct liquid forms of supercooled water [3].

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# Molecular dynamics study of curcumin in water, methanol and dimethyl sulfoxide

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Curcumin, derived from the root of turmeric *Curcuma longa*, is well known not only as a spice and natural colouring agent, but also due to pharmacological activity resulting in ample therapeutic applications. Namely, the issues concerning the antioxidant, anti-inflammatory, antiviral, anticancer activity of curcumin, its effects in chemical reactions related to Alzheimer disease and HIV-1 have become the subject of very many important experimental studies during last few decades. In the present report a model for the curcumin molecule based on the united atom OPLS-UA force field is proposed and studied by using molecular dynamics simulations in different solvents such as SPCE water [1], methanol and dimethyl sulfoxide (DMSO). We demonstrate how the considered solvents affect conformational properties of curcumin. We found that in water a curcumin molecule is more bent than in methanol and DMSO. It is related to the overall hydrophobicity of curcumin. Another effect of a solvent on the conformational properties of a curcumin molecule is in "switching" of its enol hydrogen between two positions: inward and outward the enol group leading to local changes in interaction between curcumin and solvent molecules, hence it affects the surrounding of the curcumin in this region. It is noticed that in water the probability of outward direction of the enol hydrogen is higher than in methanol or DMSO, and it slightly improves an attractive ability between curcumin and water due to a possibility to form larger number of hydrogen bonds in this conformation. It is also shown that the dipole moment of curcumin is affected by the enol group conformation. The surroundings of curcumin near the enol group as well as near a number of other groups are analyzed using the corresponding pair distribution functions and spatial density distributions of solvent molecules around the curcumin molecule. It is noticed that the density distribution of solvent molecules around curcumin molecule is highly heterogeneous due to peculiarities of interaction between its groups and solvent molecules. In water the densified regions are observed mainly near the hydroxyl groups, while methanol and DMSO molecules cover the curcumin broader and the sharp maxima of the pair distribution functions indicate an evident preference for DMSO arrangement around the entire curcumin molecule. From the dynamic properties obtained for a single curcumin molecule we conclude that the self-diffusion of curcumin in methanol is higher than in water and DMSO, and the lowest one is in DMSO. Within the framework of our study we also consider a self-assembly phenomena of a different number of curcumin molecules. A trend for the cluster formation of curcumin molecules is very well pronounced in aqueous environment. The curcumin aggregates obtained in water are analyzed in order to understand mechanisms leading to their formation, to observe mutual orientation between curcumin molecules and/or their groups within the clusters as well as to check an overall stability of the considered complexes at different conditions.

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## Liquid polyamorphism driven by interconvertible states in a single-component fluid

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“Liquid polyamorphism” is the existence of two alternative amorphous structures in a single-component liquid. Liquid polyamorphism is found in a broad group of very different materials, such as silicon, silicon dioxide, cerium, and hydrogen, usually at extreme conditions. In particular, this phenomenon is hypothesized in metastable, deeply supercooled water. The hypothesized liquid-liquid metastable coexistence is not directly accessible in bulk-water experiments because it is presumably located a few degrees below the empirical limit of homogeneous ice formation. We present a generic phenomenological approach to describe liquid polyamorphism in a single-component fluid, which is applicable regardless of the difference in microscopic origin of the phenomenon. To illustrate the approach, we consider two simple models for a single-component fluid, the lattice gas models and the van der Waals model with “chemical reaction” equilibrium between two alternative interconvertible states. This allows us to describe within the same model all the possible fluid phases (e.g. vapor and two liquids), their coexistence lines, stability limits, and thermodynamic anomalies. The results are compared with the properties of realistic water-like models, obtained by MD simulations, and with the behavior predicted in metastable deeply supercooled and superstretched water.

## A review of classical interatomic potentials applied to aqueous lithium chloride solutions

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Aqueous lithium chloride solutions up to very high concentrations have been investigated by classical molecular dynamics (MD) and reverse Monte Carlo (RMC) simulation techniques. Various force fields based on the 12-6 Lennard-Jones non-bonded model, parametrized for non-polarizable water solvent molecules (SPC/E, TIP4P, TIP4PEw) were considered. More than twenty combinations with several ionic potentials have been examined at four different salt concentrations. Densities, static dielectric constants and self-diffusion coefficients were calculated. Results derived from the different force fields were found to scatter over a wide range of values.

Neutron and X-ray weighted structure factors have also been calculated from the radial distribution functions and compared with experimental data. Particle configurations obtained from MD were refined by the RMC technique, in order to get the most accurate structural information which is compatible with X-ray and neutron diffraction experimental data, as well as with the outcome of MD simulations. Several of the investigated combinations of potential models proved to be inconsistent with diffraction data; these combinations have to be considered as inappropriate, even though not only one of them had previously been applied in computer simulations.

## On the existence of a scattering pre-peak in the mono-ols and diols

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Associating liquids, such as water and alcohols, exhibit a wealth of structural organization at the microscopic level. The existence of specific structuring in neat mono-ols [1] has been pointed out by the results of scattering experiments on those alcohols, which have revealed a pre-peak in scattering intensity [2]. With the increase of alkyl chain length, the pre-peak in scattering intensity becomes more prominent [2], showing the increase of chain-like clusters. But what happens in alcohols which have two hydroxyl groups bound by an alkyl chain?

In this work, we are looking into four neat 1,n-diols (1,2-ethanediol to 1,5-pentanediol), which were studied by means of molecular dynamics simulations. Radial distribution functions, site-site structure factors, cluster size distribution probabilities and calculated X-ray intensities are reported and compared with corresponding mono-ols [3].

It's found that in diols, just like in monools, the increase in carbon chain length leads to an increase in the hydroxyl group associations. However, our calculated X-ray intensities show that the pre-peak tends to diminish to a shoulder, which is in variance with monools. We attribute this contrasting finding to the fact that the alkyl chain is constrained between the two hydroxyl groups in linear diols, while they are free in linear mono-ols.

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## Modeling Water as a continuous medium

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Water is the most abundant liquid on Earth and is a prerequisite for life on this planet. It is also a complex fluid that exhibits many unexplained anomalous thermodynamical behaviors. In the last decades, very efficient atomistic models of water were developed to study this liquid. However, the computation time needed for these approaches is often limiting when studying water in complex 3D environments. In this work, we take a complementary approach and propose to model water as a continuous medium characterized by its density and its polarization [1]. Its physical properties are described by a Hamiltonian that we obtain by a Landau-Ginzburg expansion that reproduces the structure factor and the astonishing dielectric susceptibility of water. This approach presents several advantages: the derivation of analytical expressions for the quantities of interest such as pair correlation function as functions of a small number of parameters and a computation time significantly reduced. Our coarse-grained model is thus complementary to atomistic models. We present the model and evaluate its performance by deriving the response of the fluid to neutral and charged impurities and the hydrophobic interactions between inclusions [1].

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## Estimation of direct transition mechanism for molecular diffusion in type I gas hydrates using Density Functional Theory

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Remarkable research efforts have been performed concerning the analysis of hydrates and organic using different theoretical approaches such as molecular equations of state, molecular simulations including both Molecular Dynamics and Monte Carlo techniques, and different ab initio Quantum Mechanics approaches [1-3]. In this work, CO<sub>2</sub> and CH<sub>4</sub> type I hydrates have been studied using electronic Density Functional Theory (DFT) [4] and the Quantum Theory of Atoms in Molecules (QTAIM). Several mechanisms for transport of gases inside hydrates have been proposed so far in literature. Previous results have pointed out the apparent impossibility of some guests passing directly through faces connecting adjacent cages without destroying the water structure. Both types of cells included in the structure of type I hydrate were modeled as isolated double semi-flexible atomic systems. Interaction potentials of guest molecules with the enclathrating cell, when moving between neighbour cells were calculated using B3LYP/6-311+g(d,p) DFT approximation. Our calculations show that direct transitions are feasible through hexagonal and pentagonal faces without compromising the overall structure integrity in opposition to other results previously reported in literature. This stability has been explored using the QTAIM theory and reveals that even in the case that some bond may break during the transition, all of them are recovered, because the face distortion is absorbed locally by the hydrogen bond network. The validity of the theory level selected has been stated, and the high anisotropy of the guest-cell interaction potential for the molecules analysed is shown, which may be considered in the formulation of hydrate thermodynamic models as equations of state, and also for the description of transport properties.

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# Evaporation dynamics of inclined water droplets

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When a water droplet is placed on an inclined substrate, it can be deformed by gravitational force and its initial contact angle divides into front and rear contact angles by inclination [1-4]. Here we study on evaporation dynamics of a pure water droplet on a flat solid substrate by controlling inclination of substrate and measuring mass and volume changes with time. We find that a lifetime of evaporating droplets becomes longer as gravitational influence becomes stronger. The droplet deformation by gravity increases the difference between front and rear angles, which quickens the onset time of depinning and consequently reduces the contact radius. This result makes the longer lifetime of inclined droplets than non-inclined droplets. This finding would be important to improve understanding on evaporation dynamics of droplets under various force fields [5-7].

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# Temperature induced changes in the hydrogen-bond network of water-ethanol mixtures in the water-rich composition range

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Ethanol-water mixtures have attracted a continuous interest thanks to their anomalous behaviour in many aspects (thermodynamic and transport properties, diffusion coefficient, compressibility, viscosity). These features are reflected by their non-trivial phase diagram, as well. In these systems hydrogen bonds play a fundamental role. By means of monitoring their changes as a function of temperature one may be able to elucidate, for instance, the freezing process at the molecular level.

For this purpose we have performed a series of Molecular Dynamics simulations for ethanol–water mixtures with 10, 20 and 30 mol% ethanol content. The main goal was to reproduce X-ray diffraction data [1] at the available temperatures: 298 K, 268K, 258K and 253K (for  $x_E=0.1$ ); 298 K, 268K, 258K, 253K, 243K, and 233K (for  $x_E=0.2$ ); 298 K, 268K, 253K and 238K (for  $x_E=0.3$ ). For ethanol the All-Atom Optimized Potential for Liquid Simulations (OPLS-AA) [2] has been used in each calculation. In order to find the potentials that provide the best agreement with experimental total scattering X-ray structure factors [1] we have applied two different water force field, the Extended Simple Point Charge model (SPC/E) [3] and the improved Transferable Intermolecular Potential with four Particles (TIP4P-2005) [4]. Additionally, we have also tested the effect of the ‘flexible molecule approach’ in the case of both ethanol and water molecules.

The resulting MD trajectories have been analysed to reveal the hydrogen-bond network. Hydrogen-bonds have been identified in two ways. The geometrical consideration takes into account the non-bonding distance between an oxygen and a hydrogen atom, as well as the O...O-H angle. On the other hand, the energetic criteria are set by the O...H non-bonding interaction energy.

In the hydrogen-bonded network, cyclic and acyclic parts have been identified, and their properties have been discussed.

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## Modification of the Stokes law in confinement at the nanoscale due to memory effects

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The solvent friction experienced by a harmonically confined molecule in water is shown based on molecular dynamics simulations to strongly depend on the force constant  $K$  of the confining potential, with the friction constant  $\gamma$  reaching in the limit  $K \rightarrow \infty$  about 1.5 times the value of the free case  $K = 0$ , where the transition occurs in the biophysically relevant regime of  $K \approx (10^2 - 10^4)$  kJ/mol/nm<sup>2</sup>. This occurs despite the fact that the Stokes law predicts the friction constant  $\gamma$  to depend only on the properties of the molecule and the solvent viscosity. The transition between the two limits can be understood in terms of an additional timescale reflected in the molecule-water memory kernel, which is linked to the oscillation period in the potential.



# Activity coefficients of individual ions in multivalent electrolytes: Comparison of experiment and the II+IW theory

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It is a well-known experimental fact that the activity coefficient of electrolytes (the excess chemical potential) depends on the electrolyte concentration non-monotonically; it decreases near infinite dilution according to the Debye-Hückel (DH) limiting law, goes through a minimum, and increases at high concentrations close to saturation. Experimental determination of the mean activity coefficient from experiments is obvious, but there has been a heated debate about the measurability of the activity of individual ions. From a theoretical point of view, the individual ionic activity coefficient is a well-defined quantity.

We investigate the individual and mean activity coefficients of ions in  $X(\text{Cl})_n$  electrolytes using our theory that is based on the competition of ion-ion (II) and ion-water (IW) interactions [1-3]. The II term is computed from Grand Canonical Monte Carlo simulations on the basis of the implicit solvent model of electrolytes using hard sphere ions with Pauling radii. We also present results obtained from the Extended Debye-Hückel (EDH) theory [4]. The IW term is computed on the basis of Born's treatment of solvation using experimental hydration free energies. The results show qualitative agreement with experimental data which is remarkable considering the facts that our model does not contain any adjustable parameter. All the parameters used in the model are taken from experiments: concentration dependent dielectric constant, hydration free energies and Pauling radii.

Our results show that the non-monotonic behavior of the mean and individual activity coefficient can be explained by the balance of the IW and II interactions as two competing effects instead of the traditional view, in which the balance of hard sphere and electrostatic interactions is responsible for the effect (using an unrealistic “solvated ionic radius”).

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# Calculating the partition coefficient of pyrene and asphaltenes using computer simulations

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Asphaltenes are a fraction of crude oil that is defined as soluble in toluene but insoluble in *n*-heptane [1]. As asphaltenes are a natural product defined as a solubility class, it encompasses a huge range of possible structures that consist of fused polyaromatic rings with flexible linkers and tails. The composition and quantity of asphaltene fractions extracted varies widely with source, temperature, pressure and time. Asphaltenes are of interest to the petroleum industry as they readily form aggregates and can cause problems during oil production.

Despite the large possible number of chemical structures, asphaltenes are thought to fall into two classes; continental asphaltenes consisting of a single large polyaromatic region with flexible chains connected to the outer rings, and archipelago asphaltenes consisting of several smaller polyaromatic regions linked by flexible chains. We have initially studied pyrene (four fused rings) before considering representative asphaltene molecules of both continental and archipelago classes.

The partition coefficient, or solubility ratio between two solvents is proportional to the difference in excess chemical potential of the solute in the two solvents of interest, in this case *n*-heptane and toluene. We employ Monte Carlo simulations to calculate these excess chemical potentials and thus the partition coefficient using a coarse grained potential [2,3].

At infinite dilution the excess chemical potential is equal to  $\Delta G_{\text{solvation}}$  of a single solute molecule. Due to the dense nature of the liquid solvent and the relatively large size of the solutes it is not possible to calculate the excess chemical potential using a standard particle insertion technique, therefore we use the following thermodynamic cycle to calculate  $\Delta G_{\text{solvation}}$  by thermodynamic integration. First, we grow a cavity in the solvent, this step is common for all solutes under the same conditions. We then insert the solute into the cavity and finally shrink the cavity. By growing the solute in a cavity it alleviates any difficulties due to particle overlaps.

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## Intramolecular structure and energetics in supercooled water and aqueous solutions

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The structure and properties of water and aqueous solutions are among the most fascinating topics in natural science. They have been discussed controversially for over one century. In particular in the metastable supercooled state water anomalies become more pronounced [1], e.g. anomalous behavior of thermodynamic properties such maxima of the specific heat. Despite ongoing effort in theory, simulation and experimental work, a detailed view of the structure of liquid water and its connection to the water's anomalies is still pending.

In this contribution we present results from X-ray Compton and X-ray Raman scattering studies on supercooled water down to 255 K [2]. The oxygen K-edge measured by means of X-ray Raman scattering suggests an increase of tetrahedral order similar to the conventional temperature effect observed in non-supercooled water. Compton profile differences indicate contributions beyond the theoretically predicted temperature effect [3] and provide a deeper insight into local structural changes. These contributions suggest a decrease of the electron mean kinetic energy by  $3.3 \pm 0.7$  kJ (mol K)<sup>-1</sup>, potentially due to intramolecular structural changes reported in two-component systems [4] that cannot be modeled within established water models. These results emphasize the need for water models that capture in detail the intramolecular structural changes and quantum effects to explain this complex liquid. In addition, we discuss Compton scattering results from aqueous solutions of trimethylamine N-oxide (TMAO) and sodium phosphate (NaH<sub>2</sub>PO<sub>4</sub>) which are suggested to strengthen the hydrogen bonds of water.

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## Modelling of liquid 1,4-butanediol: Molecular dynamics and x-ray scattering studies

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Molecular dynamics (MD) simulations combined with different force fields were performed to study the structure of liquid 1,4-butanediol at 25°C. Utilizing the Complemented system approach method developed for the calculation of x-ray scattering from simulation data [1] small- and wide-angle x-ray scattering (SWAXS) intensities of model butanediol resulting from MD simulations were calculated and compared to the experimental SWAXS data. In MD simulations the Gromacs software package was applied and three all-atom (CHARMM27 [2], OPLS-AA [3], and AMBER03 [4]) and two united-atom force fields (GROMOS96-54a7 [5] and TraPPE-UA [6]) were used. Such a comparison enabled us to assess the quality of the performance of these models in structural characterization of the chosen alcohol. The simulation results show that all the tested models reproduce the basic characteristics of the experimental SWAXS curves of 1,4-butanediol, however, the best job is done by TraPPE-UA force field. This is somewhat surprising because the same models performed more alike in the case of modelling of *n*-butanol [7,8]. The simulation results were also analyzed for H-bonding characteristics and visualized via the radial and spatial distribution functions.

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## Various models for *n*-butanol: Molecular dynamics and x-ray scattering studies

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Computer simulations can provide reliable thermodynamic and structural info on modelled chemical systems only in the case when sophisticated force field models are used. A number of classic force field models are available nowadays, but they seem to show very different quality of performance in various structural studies. We have studied the accuracy of the theoretical predictions for the structure of liquid *n*-butanol at 25 °C resulting from the model calculations implemented by various force fields [1,2]. For this purpose molecular dynamic (MD) simulations of model alcohol were performed applying the Gromacs software package and the following force fields: GROMOS96-54a7 [3], CHARMM27 [4], OPLS-AA [5], AMBER03 [6], and TraPPE-UA [7]. Furthermore, the small- and wide-angle x-ray scattering (SWAXS) intensities of model *n*-butanol were calculated based on a number of noncorrelated MD configurations and were then directly compared to the experimental SWAXS data. For these calculations we have used the Complemented system approach method [8]. Since SWAXS is directly sensitive to the spatial organization of the molecules in the system, such comparison represents a stringent test for the quality of the structural performance of these models. The basic characteristics of the experimental SWAXS curves of *n*-butanol were successfully reproduced by all the tested models, even though minor qualitative to considerable quantitative discrepancies in the shape of the scattering functions were observed with different force fields and were assigned to different model parametrizations. MD simulation results are presented and discussed via the radial and spatial distribution functions and through the H-bonding data.

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# Modelling the thermodynamic properties of aqueous electrolyte solutions with a free energy perturbation approach

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Accurate thermodynamic modelling of electrolyte solutions is a challenging endeavour owing to the variety of different types of physical and chemical interactions which govern their bulk phase properties. Aside from the short-range dispersion forces and the long-range polar and Coulombic interactions which are pertinent to such mixtures, a comprehensive thermodynamic model should also account for possible hydrogen-bond formations, ion-pairing phenomena, and electrolyte dissociation equilibria.

Methods employing a free energy perturbation approach are well suited for addressing electrolyte systems with such complex interactions. One such method is the statistical associating fluid theory (SAFT) [1, 2], which is implemented in this work as a basis for modelling fluid mixtures following the first-order thermodynamic perturbation theory of Wertheim [3]. The proposed model incorporates Coulombic ion-ion interactions with the primitive unrestricted mean spherical approximation (MSA) [4], and implicitly treats ion-solvent polar interactions through the Born solvation free energy [5]. Localised charge effects arising from the structural topology of the charged species in question are accounted for effectively within the model's group-contribution approach to representing chemical entities. Application of a Mie [6] (generalised Lennard-Jones) intermolecular potential provides a representative description of the dispersion forces in the fluid mixture, while the model is completed by treatment of intermolecular association interactions via short-range bonding sites.

Focusing on aqueous electrolyte solutions, this work couples the SAFT physical model with a description of electrolyte dissociation equilibrium conditions and consequently demonstrates that a variety of electrolyte systems can be modelled successfully using a common modelling platform. Both strong and weak electrolytes are considered, achieving sound descriptions of properties such as the ionic hydration free energies, salt solubilities, and mean ionic activity coefficients, as well as bulk phase properties such as densities and saturated vapour pressures. We demonstrate the fidelity of our proposed approach by attaining excellent predictions of these properties using as little as one optimised model parameter per ion in aqueous systems, and with minimal use of experimental data input for parameter development.

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It has not been fully clarified whether water has a crucial role for the self-assembly of soft materials or it is just a homogeneous solvent without a role. Recently we have been investigating hydration states of phospholipids, the main constituent of biomembranes, using THz spectroscopy. By this method, water dynamics is precisely observed in ps time scale. In the lamellar phase of the lipids, the water layer thickness between lipid bilayers is only about 2 nm. It was found that most of the interlamellar water is regarded as a hydration water, whose rotational relaxation dynamics is slower than bulk water [1]. The hydration state depends strongly on the chemical structure of the lipid head groups [2]. The spectrum of the interlamellar water extracted by the Bruggeman's theory indicates that hydrogen-bonds are disturbed or destroyed in the layer. The hydration states of the lipids changes discontinuously at the phase transitions of the lipids, such as  $L_{\beta}$ - $L_{\alpha}$  transition.

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## Fast molecular dynamics and phase transition of water confined inside carbon nanotubes

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Single-walled carbon nanotubes (SWCNTs) provide atomically smooth nanocavities that encapsulate various guest molecules. These confined materials exhibit unusual properties that do not appear in the bulk [1]. Water was reported to have extremely high mobility inside SWCNTs, and thus SWCNTs are an attractive model system to reveal the function of hydrophobic biological channels and to design high performance filtering/separation devices [2]. Nanoconfinement suppresses water crystallization below ca. 235 K [3]; therefore, SWCNTs enable the exploration of liquid states that cannot be achieved in bulk super-cooled water.

In this study, water dynamics inside SWCNT samples with mean diameters larger than ca. 1.4 nm were investigated systematically using <sup>2</sup>H nuclear magnetic resonance spectroscopy. The results are discussed with those of differential scanning calorimetry and X-ray diffraction measurements, and molecular dynamics calculations. Fast water rotational dynamics is found to continue down to ca. 220 K in SWCNTs on cooling. On further cooling, water undergoes a first-order phase transition between fast and slow dynamics states, where the temperature is dependent on the SWCNT diameter and is extrapolated to a singularity temperature of ca. 230 K for bulk water. This observation may provide some insight into the unsolved mysterious properties of bulk water.

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## Total Neutron Scattering: the order of disorder

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Total neutron scattering (TNS) has been applied for almost 30 years at ISIS to the study of liquids and glasses. The unique combination of high energy neutrons and forward scattering detectors allows a routine  $Q$  range of 0.1-50 Å on SANDALS (TS1) and, more recently, 0.01-80 Å on NIMROD (TS2), with minimal inelasticity corrections. In the past 15-20 years, the traditional hydrogen/deuterium substitution technique has been complemented with atomistic simulations (EPSR), to allow for structure refinement and full exploitation of the diffraction data.

In three decades, the scientific program of the Disordered Materials group at ISIS has seen a dramatic increase in quantity and breath, going from water and amorphous ice to aqueous solutions of biological molecules, to clays and nanomaterials. In this contribution I will focus on materials with an application or potential application in the energy and environmental fields, showcasing some of our most recent and most advanced studies.

The study of hydrogen storage and battery materials is a key area for TNS, as many scientists turn away from classical crystalline materials to investigate the interesting properties that disordered and amorphous materials have to offer. Heterogeneous catalysis and synthesis of catalytic materials has been studied on SANDALS, making use of the ability to dose samples in situ and thus examine a catalytic reaction in its before and after states.

The investigation of ionic liquids and their application as novel green solvents is an area that has developed on SANDALS since 2007, with more and more researchers moving away from the coarse grain description provided by SAS techniques to seek a detailed understanding of the diverse molecular bonding in these solvents. More recently, studies of the emerging area of deep-eutectic solvents have also contributed to SANDALS environmental programme.

A theme that cuts across the energy and environment and manufacturing areas is the study of homogenous catalysis in water, where new compounds have the potential to substitute water for traditional solvents as a medium for chemical reactions.

## Simple models of alcohols

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Alcohols are widely used as solvents, reagents and raw material in industry. They consist of a polar, hydroxyl group, and nonpolar alkyl chain. Alcohol duality nature contributes to the complexity of the intermolecular structure. Alcohols have the ability of forming hydrogen bond networks which can lead to the aggregation of molecules in liquid phase which is different comparing to structure of water due to less hydrogen bonds and nonpolar group.

Monte Carlo simulations, performed in NPT ensemble, were used to calculate thermodynamic and structural properties of four different two dimensional models with alcohol-like properties. Alcohols were modeled as a two or three Lennard-Jones disks at a fixed separation. The first disk represents hydroxyl group which interacts through an orientation-dependent hydrogen-bonding interaction beside Lennard-Jones interaction. Other disks represent non-polar group.

We were interested in thermodynamic properties (density, molar volume, heat capacity, isothermal compressibility and coefficient of thermal expansion) as a function of temperature and in structural properties, particularly in ability to form hydrogen bonds. We also calculated pair correlation functions and did analysis of clusters.

## Properties of bulk and confined water-alcohol mixture

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Properties of liquids mixture can be experimentally investigated, however Monte Carlo (MC) and molecular dynamics (MD) simulations are important and valuable alternative as they provide detailed microscopic picture of the system. In our first study with MC method, we determined the thermodynamic and structural behaviour of a bulk simplified two-dimensional mixtures of water and methanol, and ethanol and water. These models include the qualitative features of intermolecular interactions in real systems. For water we used so called two-dimensional Mercedes Benz model that was originally developed by Arieh Ben-Naim in 1971. Water is represented as a two-dimensional disk with Lennard-Jones centre and three arms, which describe the formation of hydrogen bonds [1]. Similarly, alcohols are described by a disk with two arms to present the hydroxyl group, which has Lennard-Jones (LJ) centre, plus an additional disk for each CH<sub>x</sub> group. The simplicity of those models allows us to perform a very comprehensive study of the structural and mechanical behaviour of mixtures. In a second study, we used hybrid MC and MD simulation to investigate the thermodynamic, structural and dynamic properties of water-methanol mixtures confined within slit hydrophobic graphene nanopores. In this case we used more realistic models for water and methanol, namely, TIP4P/2005 and OPLS/2016, where the cross interactions were fitted to reproduce the experimental excess properties [2]. Investigation of properties of confined mixture, holds huge importance in scientific matters such as separation of mixture, which is our main goal [3].

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## Ammonia clathrate hydrate as seen from Grand Canonical Monte Carlo Simulations

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Overcoming the important deficiencies of the clathrate equilibrium data at low temperatures by using theoretical approaches such as the van der Waals & Platteeuw method seems truly tempting. However, this thermodynamic route is usually based on descriptions with simplified intermolecular potentials calibrated using equilibrium data obtained at high temperatures. As a consequence, the theoretical model's ability to predict the composition of clathrates in the outer Solar System could be easily questioned. In the current work, we show that Monte Carlo simulations performed on the Grand Canonical ensemble (GCMC) can be efficiently used to determine theoretically the amount of gas species trapped in the clathrate hydrates at low temperature in various situations as encountered in the Solar System.

In this study, single-guest clathrate, in particular,  $\text{NH}_3$  has been considered which is thought to contribute to the outgassing of methane clathrate hydrates into the atmosphere of Titan and Enceladus due to its role as a water-ice antifreeze and methane clathrate thermodynamic inhibitor. However, recent experimental results have indicated that  $\text{NH}_3$  clathrate of structure I could be stable at the very low temperatures typical of these Moon's atmospheres (i.e., below 150 K)[[1,2]. GCMC simulations have thus been performed to determine the amount of  $\text{NH}_3$  trapped in clathrate as a function of the partial pressure at different temperatures. The obtained results show that the strong tendency of hydrogen bond formation between  $\text{NH}_3$  and water molecules leads to the destabilization of the clathrate cages. As a consequence, stabilizing the ammonia clathrate in molecular simulations appears very challenging, indicating that this clathrate could be stable only under very specific conditions.

This application illustrates the efficiency of the GCMC method for studying gas trapping in clathrates at low temperatures of interest for planetary sciences.

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## Influence of the interaction model on dynamic properties of liquid water

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In this work, we study dynamic properties of liquid by classical molecular dynamics simulations. We investigate self-diffusion coefficient, viscosity and dynamic structure.

We compare the predictions of two rigid models of interactions, non-polarizable SPC/E (J. Phys. Chem. 91, 6269 (1987)) and polarizable BK3 (J. Chem. Phys. 138, 204507 (2013)) models.

After having discussed their respective ability to predict experimental results, we focus on the density and temperature dependence of these three properties.

## Mercedes-Benz like model for methanol

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A simplified two dimensional (2D) model for methanol is proposed and its properties studied. Model is analogous to the 2D Mercedes-Benz water model and treats orientationally dependent hydrogen bonding interactions in a similar way. Methanol molecules are described as two tangentially fused Lennard-Jones disks, one of them having two arms to account for hydrogen bonds formation. Monte Carlo simulations were done to determine thermodynamic and structural properties for a wide range of temperatures. Stable infinite chain crystal structure is maintained at lower temperatures, analogous to the structures observed in real methanol. Thermodynamic quantities, such as heat capacity, compressibility and thermal expansion coefficient were calculated from fluctuations of volume and enthalpy in the system. Results were compared with ones from molecular dynamics simulations performed with standard Trappe and OPLS models and experimental results for real methanol.

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An analogy between charge ordering in binary Coulomb fluids and micro-segregated binary mixtures is drawn, based on two observations. The first is that the microscopic distribution shows in each case alternated disposition of the two constitutive entities. The second concerns the strictly out of phase long range correlations between like and unlike entities. This analogy allows to understand the radiation scattered intensities as particular case of a generalized Bathia-Thornton structure factor, hence attributing a “valence” of the segregated domains. In turn, this interpretation allows to finally understand the experimentally known absence of pre-peak in the Xray or neutron scattering intensities of many aqueous mixtures of small solute molecules. This approach shed new light into the molecular mechanisms that allows the appearance or not of a pre-peak in scattered intensity of aqueous mixtures of large surfactant molecules.

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This study considers the aggregation properties of monoclonal antibody molecules in solution. The molecules are treated as flexible particles with spatially specific binding sites. For this purpose we construct the model in which seven equal beads are assembled together to mimic Y-shaped antibody molecules. We do this by adapting Wertheim's theory of strongly interacting particles [1, 2]. In our model the Fab–Fab and Fab–Fc terminal interactions can yield to the self association. The free energy of such one-component fluid has the hard-sphere and the association term. The results will be presented for the cluster size distributions and their impact on fluid viscosity.

The results indicate that Fab–Fc terminals association yields higher viscosity than the Fab–Fab type. Interestingly, the bi-specific antibodies, in which a single antibody molecule binds two different epitopes [3], can have more controllable viscosity properties than traditional monoclonal antibodies. The second virial coefficient is calculated and correlated with the viscosity measurements.

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## Molecular dynamics simulation of a binary mixture near the lower critical point

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2,6-lutidine molecule mixes with water at high and low temperatures but in a wide intermediate temperature range a 2,6-lutidine/water mixture exhibits a miscibility gap. We have constructed and validated an atomistic model for 2,6-lutidine and have performed molecular dynamics simulations of 2,6-lutidine/water mixture at different temperatures. We have determined the part of demixing curve with the lower critical point. The lower critical point extracted from our data is located close to the experimental one. The estimates for critical exponents obtained from our simulations are in a good agreement with the values corresponding to the  $3D$  Ising universality class [1].

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## Phase behaviour of a core-softened fluid from the chemical potential perspective

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In a tetrahedral liquid the local (short-range) order around a particular molecule center is tetrahedral and is a consequence of the nature of the underlying interactions between fluid molecules (for example, hydrogen bonding in water) [1, 2]. Water anomalies are a consequence of the competition between the tetrahedral order (promotes the formation of low-density/low-entropy structures) and pair (translational) order (promotes the formation of dense phases) [3]. Isotropic core-softened potentials were proposed to study the properties of tetrahedral liquids. These potentials are characterized by two repulsive parts and the ratio between these “hard” and “soft” repulsive length scales is responsible for anomalous behaviour [4]. Besides gas-liquid phase transition, these models can exhibit also low density liquid-high density liquid phase transition [5].

In this contribution the phase behavior of the continuous shouldered well model fluid first proposed by Franzese [6] will be examined using the Monte Carlo computer simulations in the canonical and grand canonical ensemble [7]. Integral equations will be used to explore certain parts of the phase diagram. The insights into the phase behaviour of the model will mainly be gained from the perspective of the chemical potential as the external parameter. The essential parts of the vapour-liquid and liquid-liquid coexistence envelopes will be presented. The Widom lines departing from coexistence envelopes will be calculated from the maxima of particle number fluctuations as a function of chemical potential along various isotherms. The excess pair entropy will be used for locating the region embracing anomalies in the properties of the model. The temperature of maximum density line will be calculated. The results will be compared with the ones from molecular dynamics simulations.

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## Adaptive resolution simulation methods: fundamental aspects, applications, and perspectives

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Adaptive resolution simulation methods [1, 2, 3] concurrently employ different descriptions of a given system, typically a fluid, in the same setup: a detailed and computationally expensive model –e.g. fully atomistic– is used to represent a small yet relevant subpart of the system, while the rest is treated with simplified, coarse-grained interactions. A key feature of these approaches is that the boundary separating the two simulation box subregions is *open*, thus allowing molecules to diffuse freely across it.

Here, I will provide an overview of the Adaptive Resolution Simulation (AdResS) [1] and the Hamiltonian AdResS (H-AdResS) [2, 3] methods, ranging from the fundamental theoretical aspects to the most recent developments and applications for the study of thermodynamical properties of liquids and biomolecules [4, 5, 6]. Particular prominence will be given to the current implementation in freely accessible software [7] and the future directions of the method.

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## Equilibrium properties in the thermodynamic limit from small-sized molecular dynamics simulations

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In this talk, we present an accurate and efficient method to obtain equilibrium thermodynamic properties of bulk systems from small-sized molecular dynamics simulations by introducing finite size effects into integral equations of statistical mechanics. We validate the method by calculating thermodynamic properties of prototypical complex mixtures such as the activity coefficients of aqueous urea mixtures and the Kirkwood-Buff integrals of Lennard-Jones fluids. Moreover, our results demonstrate how to identify simulation conditions under which computer simulations reach the thermodynamic limit [1].

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## Calculation of Excess Chemical Potential of Liquids via Hamiltonian Adaptive Resolution Simulation

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The calculation of chemical potential of liquids is a relevant and challenging problem in computational chemistry and physics. Employing the multi-scale Hamiltonian Adaptive Resolution Simulation (H-AdResS) [1, 2] method, we propose a method to calculate the excess chemical potential of dense liquids. In H-AdResS, the simulation domain is subdivided in regions of high and low resolutions, coupled through a hybrid region. Since the dynamics of particles are obtained from a global Hamiltonian, the generated statistical ensembles of the system are well-defined. Here, the fluid within the high resolution region is coupled with an ideal gas of non-interacting particles, and to enforce a uniform density profile an external force is computed on-the-fly and applied. The potential energy of this external field is related to the Gibbs free energy difference between the two resolutions, which allows one to obtain from it the excess chemical potential of the fluid with respect to the ideal gas. We validated this method by calculating the excess chemical potentials of model systems and realistic aqueous solutions.

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Liquid water is characterized by a number of striking anomalies in the thermodynamic response functions suggesting an apparent singularity at a temperature estimated at  $\approx 228$  K. Yet what sort of singularity might water be approaching still represents an unresolved puzzle because of the enormous challenges that prevent the direct experimental access to the liquid water properties below a temperature of  $T_H \approx 235$  K. The use of a microscopic liquid jet of water droplets that rapidly cool by surface evaporation offers an enormous potential to the study of supercooled liquid water. Indeed, this strategy has been exploited recently to investigate the structure of supercooled water in the region below  $T_H$  [1]. However, one major drawback of this approach is represented by the intrinsic difficulties of a reliable determination of the temperature of micrometer-sized liquid droplets in vacuum. Here we show that Raman spectroscopy of the vibrational O–H stretching band allows to determine the droplet's temperature to a very high level of accuracy. We found in particular that  $6360 \pm 20$  nm-diameter water droplets were able to supercool to a lowest temperature of  $229.5 \pm 0.1$  K. Our results indicate a continuous trend in the evolution of liquid water's hydrogen bonding network extending to temperatures well below  $T_H$  with no evidence for a liquid structural transition. Furthermore, the liquid water temperature established here is not consistent with the droplet temperature estimations reported in Ref. [1], thereby questioning the interpretation of recent experimental data obtained by using a liquid water droplet beam [2, 3].

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We investigate the effect of the different organic co-solutes urea, guanidinium chloride, TMAO and ectoine on water dynamics [1] by means of molecular dynamics simulations, with the focus lying on dielectric relaxation spectroscopy. The good agreement with experimental data allows us to further investigate detailed concentration-dependent structural and dynamic properties such as tetrahedral order parameters and hydrogen bond dynamics, which are inaccessible to the experiment. Our findings exhibit distinct effects for protein protectants and denaturants, complementing previous experimental findings [2].

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# Ice nucleation near the liquid-liquid critical point in simulations of supercooled water

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Computer simulations of the ST2 model of water have demonstrated a well-characterized liquid-liquid phase transition (LLPT) [1, 2] in the supercooled region of this model's phase diagram [3]. However, the influence of the LLPT on the nucleation of ice in this model has not been quantified, in particular, the influence on the height of the nucleation barrier. Using umbrella sampling Monte Carlo simulations, we present estimates of the free energy barrier for ice nucleation near the Widom line [4], as well as our results for the barrier close to the LLPT itself [5]. We find that the nucleation barrier decreases, but does not vanish, on approaching the LLPT, consistent with previous results that show that the LLPT is distinct from the liquid-to-ice transition in ST2 water. However, the height of the nucleation barrier near the the LLPT is low, and may reach values as small as  $10kT$  to  $15kT$  at the critical point. While a barrier of this height is sufficient to make ice nucleation infrequent in a small system on simulation time scales, it is not sufficient to suppress ice formation under typical experimental conditions. These results illustrate the scenario in which a LLPT exists in the free energy surface of supercooled water, but is in practice unobservable in bulk samples due to rapid ice crystallization. We also present evidence that throughout the supercooled region, including near the melting line, small subcritical ice nuclei are surrounded by a significant region of low density liquid, which grows in extent as the LLPT is approached. This observation supports the view [6] that low density liquid fluctuations play an important role in the early stages of ice formation.

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# Fast and accurate prediction of solvation free energies of proteins

## The Molecular Density Functional Theory

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The organization of solvent molecules around proteins plays a key role in their activity and stability. Molecular simulations such as molecular dynamics are able to predict solvation properties, but with high numerical cost, e.g., several thousands of hours to study the solvation of the smallest amino-acids. We propose the Molecular Density Functional Theory, MDFT. This method, based on rigorous liquid state theories, predict in few minutes only the solvation free energy and associated density profiles for compounds of any size and any shape. First, I will present our last extension of the theory for hydrophobic systems of any size. Then, I will show the solvation free energy and density profiles of proteins.

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## The surface affinity of the hydrated proton calculated by thermodynamically consistent simulations

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In water, adsorption of ions – and in particular protons – at the surfaces of colloids, membranes and biological molecules governs the stability of colloidal suspensions, biochemical interactions and nanoparticle assembly. For over a century, however, the affinity of protons for hydrophobic surfaces, such as oil droplets and air bubbles, has been the subject of a fundamental experimental controversy: surface tension measurements show a positive surface excess of protons, whereas kinetic experiments suggest a negative surface charge density.

Here, we study the surface tension of the air-water interface, it being the simplest and most fundamental of aqueous interfaces. For the first time, we calculate the surface propensity of acids and bases at the air-water interface from thermodynamically consistent molecular dynamics simulations. The results unequivocally establish the proton surface adsorption, in quantitative agreement with surface tension experiments. We also extract the physical mechanism responsible for the differences in surface adsorption between the different ions, presenting an important step toward the resolution of the century-old ion adsorption controversy.

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Within the modern molecular-based equations of state, the Statistical Associating Fluid Theory (SAFT) [1] been the basis of multiple popular models to describe the behaviour of complex fluids [2, 3, 4, 5]. However, it remains an open problem to effectively enhance this perturbative approach to provide accurate predictions where complicated potentials are necessary to describe intermolecular interactions.

In this project we implement a thermodynamic integration approach by introducing a coupling parameter to integrate between a reference system (e.g. the hard-sphere fluid) and the corresponding real system of interest. This coupling approach has been used extensively in the study of anisotropic fluids to develop models with orientation order parameters [6, 7]. Our goal is to understand the various approximations of the high-temperature perturbation contribution, commonly employed in SAFT-type equations of state, with the aid of the explicit expression obtained from the coupling approach. This will lead to the development of a thermodynamic description for fluids that are characterised by the existence of complicated intermolecular forces, such as dipoles or liquid crystals.

In order to compare this approach with previous work we will first apply it to simple model systems. The Mie and the Square-Well fluid are two cases that have been thoroughly studied [5, 8] and are ideal as benchmarks. Once we have a good assessment of our coupling approach we intend to attempt systems characterized by more sophisticated potentials like dipole-dipole interactions.

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## Competition between inter- and intramolecular association within a SAFT framework

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The SAFT equation of state [1, 2, 3, 4] constitutes one of the most sophisticated and successful molecular-based approaches for the prediction of thermo-physical properties in industrial applications. However, most versions of SAFT are based on Wertheim's first-order thermodynamic perturbation theory (TPT1) [5], and as consequence, the formation of any type of ring, i.e., by covalent bonding, or inter and intramolecular association is neglected. The applicability of SAFT in its standard formulation is, by effect, limited to systems where these effects are not significant.

Although the extent of intramolecular association alone is a weak function of density, when the competition of this effect with intermolecular association is considered, the dominant association type is sensitive to the density. For instance, if we consider a pure fluid, the intramolecular association is expected to gain relevance with decreasing density, due to the intermolecular distances being larger. Sear and Jackson [6] and Ghonasgi et al. [7] developed theories to account for intramolecular in addition to intermolecular association, following the original theory of Wertheim [5].

In the current work, intramolecular association is considered in an explicit manner. By extending the theory of [6] to multiple associating sites and component mixtures, the SAFT framework can be modified to account for the competition between intra and intermolecular association. The results of the prediction of thermodynamic properties using SAFT for systems accounting and neglecting ring formation are discussed.

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## Viscosity in supercooled water-glycerol solutions

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Many of water's physical properties are anomalous compared to other liquids. One possible interpretation of these anomalies is a putative liquid-liquid transition between a low-density and high-density phases. Nevertheless, the transition is predicted to lie in the supercooled region, and even below the homogeneous nucleation. The transition might become experimentally observed in water-glycerol mixtures [1], which motivates our study on these solutions in their supercooled state.

We report their viscosity in a concentration range from 0 to 50% in mass of glycerol. The viscosity is measured with a method based on differential dynamic microscopy [2] [3].

We particularly discuss whether the viscosity of these mixtures in the supercooled region follows a Vogel-Tammann-Fulcher law, like fragile liquids [4], or a power law like pure water [3].

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## Probing the equation of state of deeply supercooled TIP4P/2005 water with nanodroplets

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We carry out extensive molecular dynamics (MD) simulations to study the equilibrium properties of water nanodroplets modelled with the TIP4P/2005 potential. We study a range of droplet sizes from  $N=64$  to 2880 with temperatures ranging from  $T=180$  K to 300 K. At low temperatures, we run an ensemble of  $\sim 1000$  MD simulations at individual state points to calculate equilibrium properties. We find that the droplet must be of size greater than 360 molecules to show anomalous density behaviour, i.e., droplet expansion on cooling. We calculate the local density and pressure in the droplets at all  $N$  and  $T$ . Owing to the Laplace pressure, for sufficiently small droplets, the density inside the droplet exceeds the density of water at the liquid-liquid critical point proposed for the model. With nucleation suppressed by small system size, we find the equation of state for the liquid in droplet form and compare it to that of bulk water. The comparison yields a quantitative measure of the effectiveness of using nanodroplets to probe the existence of a metastable liquid-liquid critical point and associated anomalies.

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A number of promising novel technologies can be thought of as the result of functional materials based on the interface formed between organic (bio)molecules and solid-state materials such as surfaces, nanoclusters, and nanoparticles. The properties of these interfaces are the result of a complex interplay of diverse physical-chemical interactions. In this context, theoretical and computational approaches, such as all-atom simulations based on molecular mechanics, are called to complement experiments and shed light on the involved processes at the nanoscale [1, 2].

Among these materials, gold nanoparticles have received much attention due to their potential many applications in catalysis, medical diagnostic and treatment technologies such as drug delivery, bioimaging, and biosensing for example [2]. However, the interfaces formed by gold nanoparticles are potentially quite complex due to the presence of dispersion interactions, possible weak covalent bonds, and image-charge effects due to the presence of almost-free electrons. These effects raise difficult theoretical challenges to describe the resulting metal-nonmetal interface in all-atom simulations using classical force fields.

We present our first efforts to benchmark several methodologies to describe, as a first step, the interface formed between gold nanoparticles and liquid-phase water with molecular dynamics using classical force fields. In particular, we show the resulting structural features of an icosahedral gold nanoparticle embedded in water using the METAL force field proposed by Heinz and coworkers [3] and the force field proposed by Dou and coauthors [5]. Our aim is to eventually include the high polarizability of the gold nanoparticle to fully describe the interfacial structure of the system [5, 6].

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## Bulk melting of water ice

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Apart from its rich phase diagram of thermodynamically stable phases, water ice can also be found in glassy phases called amorphous ices. While often produced by rapid cooling, such ices also form when hexagonal ice cooled to 77 K is subjected to pressures on the order of 1 GPa in a process called pressure induced amorphization (PIA)[1]. Based on experimental evidence as well as on results from molecular simulation, multiple transition mechanisms have been proposed for this process: thermal and mechanical melting, as well as a cross-over scenario between the two [2, 3]. However, direct simulations suffer from an inherent bias towards mechanical melting due to the disparate timescales accessible in simulation and experiment.

We approach the subject of PIA by studying bulk-melting in water ice, which, in the context of the thermal melting scenario, crosses over into the ice-amorphous ice transition as we follow the coexistence line towards high pressures and low temperatures. We use computer simulations employing the TIP4P/Ice water model [4] to sample dynamic trajectories of melting events and subsequently analyze them, focusing on the mechanism with which they proceed. In particular, we focus on the initial stage of defect formation, in order to identify the typical reaction channels through which this transformation proceeds.

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# **Topic 3**

## **Liquid Crystals**

## Heat-driven micro turbines with chiral liquid crystalline droplets in an oligomeric solvent

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Selection of working fluids strongly contributes to the performance of heat engines. For example, in general mechanical turbine systems, rotative powers are obtained by the flows induced by heating and cooling, and their performance strongly depends on the properties of the working fluids, such as combustion efficiency, volume compressibility, and so on. In the typical heat engines, the systems are composed of fluids and solids. In contrast, what we focus on in this presentation is the heat-driven mechanical rotations in the complex system composed only of fluidic materials, i.e. liquid and liquid crystals. However, here we show that the physical properties of the rotational phenomenon in the present fluidic system also significantly depend on the selection of the surrounding fluid similarly to the heat engines.

Recently, it has been reported in the thermally coexistence state of the cholesteric(Ch) and the isotropic (I) phases, that the rotational motions are induced in the Ch liquid crystalline droplets under temperature gradient [1, 2]. In addition to these reports, more recently, we found that convective flow was induced in the Ch droplets under such a gradient. From these results, we considered that the rotational motion would be driven by this convective flow: we expected that the structure embedded in the Ch droplet rotated owing to the flow induced by heating and cooling, just like the mechanical turbine system.

Here, we considered that the rotational behavior should strongly depend on the component materials flowing in the sample if the above consideration is valid. So far, the rotational phenomenon has been typically performed with single mixtures of several liquid crystalline molecules in the transient state between Ch and I phases, so that the droplets and the isotropic medium outside were of the same liquid crystalline mixture. In contrast, in this study, we made the Ch droplets dispersed in an isotropic oligomeric solvent PF656 (Omnova solution inc.), and succeeded in inducing the rotational phenomenon under the temperature gradient. Moreover, it was found that the induced rotational speed was several to several tens times faster than that observed in the previous works based on single mixtures.

In addition, the interior structures of the droplets also changed from the droplets observed in the transient state. We found that 7 different topological types of droplets appeared, and succeeded in switching them by changing the droplet size, strength of chirality, and heat flux. Furthermore, we clarified the internal director field in all of those 7 types of droplets, analyzing them with confocal fluorescence microscopy. The detail of them will be reported in the presentation.

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## Electro-driven director-deformation wave propagating in chiral liquid crystals confined to pillar geometries

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Cholesteric (Ch) liquid crystals (LC) have a spatially periodic structure where the director field twists along their helical axes. In this work, we found that wave propagation of periodic director deformation was generated by an alternating-current (AC) electric field to a Ch LC system

We made the droplets using the Ch liquid crystals in an isotopic liquid of fluorinated oligomer PF656 (Omnova Solutions Inc.). Using ITO-sandwich cells, we applied the electric field to the droplets. In this study, since we only focused on the Ch droplets whose diameters were 3–10 times larger than the cell thickness, they should be cylinders rather than spherical droplets. The cell substrates were coated with a fluorinated resin, CYTOP (Asahi Glass Co., Ltd.), which induced strong homeotropic anchoring. Thus, in the droplets, the fingerprint textures, which were often observed in the Ch liquid crystals under the homeotropic anchoring condition, were observed. Here, adjusting the AC electric field to a certain frequency region (~20–2000Hz), we found that the periodic waves with the propagations of the director deformation were generated.

By careful observation, it was found that there are two directional modes of propagation, namely, linear and radial propagations were mainly induced. In the latter mode, spiral structures with trifold rotational symmetry were dominantly constructed, simultaneously with the induction of the rotation of the director field. The cyclic period of these two propagation modes agreed with each other, and they didn't depend on the cylinder diameter. This result suggests that the physical mechanism of the wave generation is common in these two modes.

The cyclic period was inversely proportional to the applied voltage. In addition, we did the same experiment with the sample with some extent of an ionic impurity, TBAB (Sigma-Aldrich Co. LLC.), and then found that the frequency region of the wave generation was shifted to ~200–20000Hz. These results imply that the internal ionic flow driven by the electric field generates the wave phenomenon.

On the basis of the experimental results described above, we theoretically analyzed the stability of the spiral structure with the trifold rotational symmetry which show the radial wave propagation, using Onsager's variational principle [1]. As a result, it was found that viscous dissipation was minimized when the trifold structure was realized, suggesting that the trifold structure was selected by the minimization of the dissipation. The detail of the analysis will be reported in the presentation.

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## A study of nematic wetting near free surfaces

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In order to describe ordering of a nematic liquid crystal near a free surface, we consider a 2-d system of rods at finite temperatures, in which only excluded volume interactions are taking into account; these rods may or may not be anchored to a surface.

This system can be mapped onto a 3-state Potts model. In that order, we consider a semi-infinite 2-d system on a lattice and use a mean-field free energy [1] to describe it (generalization to 3-d is straightforward); minimization of this free energy leads to a set of recurrence relations for the layer dependent order parameters. This set is solved numerically and we obtain the profile for various cases: planar and homeotropic anchoring in flat and curved surfaces (which is reproduced through a tunable interaction profile).

Very interesting results have been obtained, including simple wetting and the onset of a finite plateau which may or may not disrupt into real wetting. This work is able to describe a new class of experiments where nematic ordering is observed in various confining geometries [2].

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## Smectic monolayer confined on a sphere: topology at the particle scale

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The impact of topology on the structure of a **smectic monolayer confined to a sphere** is explored by particle-resolved computer simulations of hard rods. The orientations of the particles are tangential to the sphere and either free or restricted to a prescribed director field with a zonal-like or meridional-like topology. Depending on the imprinted topology, a wealth of different states are found including an equatorial smectic with nematic or isotropic caps, a broken egg-shell structure of two smectics, and a situation with 4 or 6 half-integer topological defects. It is also shown that the applied directional force strongly affects the particle density on the spherical surface: in zonal like orientation the maximum density arises in the equatorial area leaving the cap areas mostly empty from the rods. These states are verifiable experimentally, e.g. in Pickering emulsions of droplets with colloidal rods.

## Programmable pattern formation in anisotropic liquids mediated by topological defects

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Pattern formations in nature, from plants or animals to cosmology, primarily arise from the inherent non-equilibrium processes [1]. Soft matters such as fluid materials and colloidal self-assemblies act as useful model systems to reproduce the counterparts. More specifically, the anisotropic fluids, i.e. liquid crystals (LCs), have been attracting much attention in pattern formation, due to their perplexing responsivity to external fields such as electric field, magnetic field and so on [2]. Various patterns induced by using external fields (mainly by electric field) have been reported in non-equilibrium states [3], many of which mimic the ones in nature. However, in general, patterns cannot persist without energy feeding because of the inherent instability in the thermal equilibrium state.

Herein, we present a new pattern formation mechanism, which involves a series of physical processes of manipulating and of stabilizing the so-called topological defects in LCs [4]. In short, we confine the massing with densely concentrated topological defects within a narrow boundary region between two distinct phases. By manipulating the boundary to sweep over the plane under an appropriate condition, the topological defects are assembled into particular ordered patterns in accordance with the condition. The proposed method has three distinct properties: (1) there is no need to use any template material for pattern formation; (2) the processes are purely physical interactions between topological defects; (3) the created patterns are stable in the thermal equilibrium state, and can be erased and recreated by external fields in facile ways. Usually, if a dense number of topological defects are present, they tend to annihilate themselves due to the energetic penalty of the high elastic strain. Our new method for pattern formation goes beyond this perspective, and hence the physical reasons of the present pattern formation might make a significant advance in stabilization mechanism in the collective behaviors of topological defects. This may also pave a new pathway to fabricating/programming ordered patterns in a repetitive manner by using LC states.

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# Unusual temperature dependence of anchoring torque in liquid crystals triggered by surface-localized structures

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When nematic liquid crystals (NLCs) are subjected to temperature reduction, they become more strongly anchored onto surfaces. Namely, anchoring coefficient  $W = K/\lambda$  (where  $K$  and  $\lambda$  are the elastic constant and extrapolation length respectively), increases with decreasing temperature. This phenomenon has been intensively studied and is ascribed mainly to the enhanced order parameter because of the increased NLC-surface interactions upon cooling. However, several outliers, which seem not to follow this rule, are puzzling for understanding the anchoring behaviors in LCs. For example, in literature [1,2], a phenomenon, dubbed as anchoring transition (ATr), presents macroscopic NLC orientational variations in response to temperature in either continuous or discontinuous manners. Recently, we found that, upon a discontinuous ATr from planar (P) to vertical (V) states in a NLC on a perfluoro amorphous polymer surface, thermodynamic creation and growth process of surface-localized smectic-A wetting sheets (SSWS) within P state plays a significant role in the bulk NLC orientation [2, 3]. It is worth noting that SSWS prefers V orientation on surface, as evidenced by grazing incident x-ray diffraction. Therefore, it is reasonable to assume that a pair of temperature-dependent competitions, between V orientation easy axis in SSWS and P orientation easy axis elsewhere all over the cell, dictates the variation of  $W$  with temperature.

Here, we present that the above-mentioned ATr results from a 'negative' temperature-dependent anchoring behavior. That is, contrary to conventional anchoring behavior of NLCs,  $W$  decreases (or  $\lambda$  increases) with decreasing temperature. By a series of various experimental methods (spectroscopic reflection ellipsometry, surface-induced second harmonic generation, grazing-incident x-ray diffraction, etc.) and the free-energy calculation based on the experimental results, we reach the conclusion that the dependence of  $W$  (or  $\lambda$ ) can be well explained by the dual-easy axes competition mentioned above.

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## Liquid crystalline properties of chain complexes based on dinuclear ruthenium carboxylates

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There have been considerable interests in the coordination chemistry of metal carboxylates with a lantern-like structure, because they have a unique dinuclear structure with metal-metal bonds. Especially dinuclear ruthenium carboxylates have attracted much attention during the past decades due to their intriguing magnetic properties, having two or three unpaired electrons in the metal-metal bond orbitals [1]. Diffused reflectance spectra show a characteristic band due to metal-metal bonds around near-IR region in these systems. Dinuclear ruthenium systems are paramagnetic and temperature dependence of their magnetic moments reveals zero-field-splitting of dinuclear ruthenium unit. Combination of magnetic exchange interaction between dinuclear units and zero-field-splitting effect may give us new aspect of magnetic materials. Therefore we have engaged in synthesis of new polymeric compounds based on dinuclear ruthenium carboxylate by use of linking ligands such as pyrazine [1]. Up to now lots of work have been carried out to study magnetic properties of dinuclear [1,2] and polynuclear systems, which showed antiferromagnetic, ferromagnetic, and ferrimagnetic behaviors [1,3-5]. Polynuclear metal carboxylates have potential application not only for magnetic materials but also for liquid crystalline materials when proper organic groups are introduced. Dinuclear ruthenium benzoate is a useful dinuclear unit to add more than one long alkyl chain groups. So, we prepared some chain complexes of ruthenium 3,4,5-trialkoxylbenzoates and investigated liquid crystalline properties as well as spectral and magnetic properties [3-5]. The liquid crystalline behavior was observed by differential scanning calorimetry and polarized microscopy for  $[\text{Ru}_2(3,4,5-(n\text{-C}_8\text{H}_{17}\text{O})_3\text{C}_6\text{H}_2\text{CO}_2)_4(\text{OCN})]_n$  [3]. These results will be discussed with those of the related polymeric compounds of ruthenium carboxylates.

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# Structure, Dynamics and Phase Behavior of a Discotic Liquid Crystal Confined in Nanoporous Anodic Aluminum Oxide Membranes

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Discotic liquid crystals (DLCs) are a promising class of soft matter for electronic applications. This is due to their ability to organize and stack themselves into columns in a hexagonal columnar mesophase, a mesophase in between the plastic crystalline and isotropic phase, driven by the overlap of the  $\pi$  orbitals of their aromatic core. This leads to a high charge-carrier mobility along the column axis. Further, these columns could then be considered as “molecular nanowires” [1].

Spatial confinement of soft matter in nanoporous media influences its structure, thermodynamic properties, and mobility [2]. Embedding liquid crystals and polymers into nanopores of anodic aluminum oxide (AAO) results in a 2D nanoconfinement of these materials. This confinement affects their properties, compared to the bulk, such as phase transition temperatures and enthalpies, molecular mobility, and architecture of the crystallization [3,4,5].

In this study, 2,3,6,7,10,11 hexakis[hexyloxy] triphenylene (HAT6), a triphenylene-based DLC, was confined into nanoporous AAO membranes. The structure, dynamics and the phase behavior of the confined HAT6 were investigated by broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC). HAT6 was embedded into nanoporous AAO membranes by melt infiltration in the isotropic phase under argon atmosphere. The membranes have parallel aligned cylindrical nanopores, with different pore diameters in the range of 10-180 nm. Bulk HAT6 forms a hexagonal columnar phase; in between the isotropic phase above 371 K and the plastic crystalline phase below 340 K. Unlike the bulk, the confined HAT6 split the phase transitions in two or more, which might be interpreted as different phase structures; close to the wall and at the pore center. Moreover, the phase transitions of the confined HAT6 shifted, with decreasing pore diameter, to lower temperatures. The dependencies of the phase transition temperatures on the pore size was well-described by the Landau-de Gennes model. Furthermore, pore surfaces of a series of membranes were chemically modified, resulting in a more hydrophobic pore surface than the unmodified ones. HAT6 was embedded into the modified membranes by the same aforementioned preparation. The influence of the changed host-guest-interaction, on the structure, dynamics, and the phase behavior of HAT6 confined in the modified membranes, was also investigated by BDS and DSC.

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## Monte Carlo studies on the phase behavior of model chiral liquid-crystals using the hybrid anchoring approach

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Since their first discovery in 1888, many industrial products have been developed to take advantage of the unique optical characteristics of liquid crystals. It is well known that liquid-crystal phases are created due to the collective behavior of rod-like or disk-like molecules under certain conditions. Subtle features at a molecular scale can give rise to many derivative phases. For example, the chirality of rod-like molecules sometimes leads to the formation of helical structures with large-scale pitch distances. These are called chiral liquid-crystal phases and have been the subject of much attention for their use in commercial applications and relevance to biological systems.

Molecular simulations using simple coarse-grained models, such as the chiral Gay-Berne model [1], are useful to understand the molecular-scale phase behavior. However, there are some difficulties in studying the bulk state for chiral liquid-crystals. Three-dimensional periodic boundary conditions are often used in such simulations to represent a bulk state, but they sometimes induce serious artifacts due to inappropriate periodic images, unless the box length along the twisted axis is an integer of half the pitch distance. In this research, therefore, preliminary simulations were performed with hybrid planar anchoring [2] in order to estimate the pitch distance for each condition. After trimming the simulation box length to an integer number of half pitch distances, long MC simulations were then performed with standard periodic boundary conditions to obtain equilibrium conditions, and the phase behavior was studied.

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## Extensional Rheology of Liquid Crystal Fibers

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It is now known that certain liquid crystal phases, namely the ferroelectric  $\text{SmC}_s\text{P}_f$  (B7) phase formed by certain bent-core mesogens, are capable of spontaneously forming stable microfibers under uniaxial extension [1,2]. These fibers, which possess a complex, layered structure, are capable of suppressing the Rayleigh-Plateau instability by means of a smectic layer compression modulus [3]. Previous studies focused on measuring the static tension of both single fibers and fiber bundles to better understand their structure and stability [4]. However, their dynamic properties were not investigated in detail until a recent publication reported on their rupture and recoil behavior [5].

In our present work, we use extensional rheometry to investigate the strain and strain rate dependent stress response and the induced structural (phase) changes of these fibers to develop a more complete viscoelastic model. Along with a better understanding of the interplay between the fluid and elastic properties of these fibers, we hope to exploit their polarization modulated nature to achieve actuation, or controlled length contraction and dilation, in the presence of external fields to produce soft, self-healing fiber actuators to be used in applications such as soft-robotics.

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## Ultraviolet irradiation caused structural transitions in nematic liquid crystal droplets

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In our contribution we study experimentally and theoretically ultraviolet (UV) caused structural transitions of liquid crystal (LC) droplets where we focus on key mechanism triggering these transformations. Recent years witness increased interest in nanoparticle or UV-irradiation driven macroscopic configurational changes in soft matrices which potentially offer numerous applications, particularly in emerging nanotechnology and biotechnology. For this purpose LC matrices are often used [1,2,3]. Namely, in addition to their liquid character, optical anisotropy and transparency, which makes them experimentally accessible, they are also strongly responsive to even weak local perturbation. We used ZhK 440 LC which exhibits trans-cis isomerization when exposed to UV irradiation. Structures within LC droplets were visualised by means of polarization microscopy. In absence of UV irradiation droplets exhibit bipolar-type structures. We observed that after the critical irradiation time  $t_c$  the radial configuration is established. Our experiments show that  $t_c$  increases with droplet radius and decreases with intensity of UV irradiation. We developed a simple phenomenological model using which we qualitatively reproduce obtained results.

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## Topological defects and structures formed by defects in smectic films in free and confined geometry

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Orientationally ordered liquid crystals possess different types of unusual and intriguing topological defects. Besides fundamental interest in their characteristics and properties, topological defects play a crucial role in various processes such as self-organization of inclusions in liquid-crystalline media.

In this work we study defects in two-dimensional orientational field of free-standing smectic films using high-resolution polarised and depolarised optical microscopy. Results of investigations of topological defects in nonpolar and polar smectic films are presented. Despite reduced dimensionality, topological defects in the films exhibit richness of configurations. We investigate free defects and defects in confined geometry of smectic islands. In the latter case rigid anchoring on the island boundary allows the existence of different types of topological defects and their topological charges. Different configurations of the director field and different number of defects can be realized. The equilibrium structure depends on layer ordering, boundary conditions and anisotropy of two-dimensional orientational elasticity [1-3]. We discuss similarities and differences of the investigated system with three-dimensional nematic and other systems of confined geometry for topological defects, such as nematic or cholesteric shells. Energies of different director configurations formed by topological defects are calculated. The equilibrium director configuration can crucially depend on the anisotropy of orientational elasticity. The results of calculations are compared with experiment. We describe formation of linear and two-dimensional structures from ordered point topological defects and walls in free-standing films.

Our findings underline the important role which can be played by topological defects in systems of confined geometry and demonstrate how defects can serve as unit elements in formation of complex unique organized structures in liquid-crystalline systems.

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## Long-period polar structures in smectic liquid crystals

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Smectic liquid crystals having layered structure form a number of polar phases [1]. In recent years polar smectic structures with long-range period were discovered and attracted close attention of experimentalists aimed to search for new multilayer structures [2-5]. These experimental findings stimulated extensive theoretical studies. Calculation of the structures, determination of interactions responsible for their appearance, description of temperature sequences of phases are a challenge for the theory of polar liquid crystals [6-8]. Calculations with only short-range interactions of adjacent layers and frustrating interactions of next nearest layers give for multilayer structures larger energies than for simple structures or the same energy in special points of the phase diagrams. In such a situation even weak factors such as presence of long-range interactions or the possibility to change the order parameter can lift the degeneracy and stabilize certain multilayer polar structures.

We performed calculations of polar smectic phases on the basis of Landau theory of phase transitions with a two-component order parameter. The model can describe not just the structures and their characteristic features, but also the temperature sequences of phases observed in experiments. In particular we calculate and investigate the physical reasons of appearance of several polar smectics with periodicity of six layers. From comparison of the experimentally discovered structures with results of calculations, interlayer interactions responsible for formation of different phases were determined. Moreover, temperature sequences of polar structures including different multilayer phases have been calculated and are in agreement with experiment.

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## Molecular ordering lowers cavitation threshold in complex anisotropic liquids

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Cavitation, often known for its deleterious effects, is a routine fluid mechanical phenomenon, in which low density vapor phase nucleates within liquids under tension – for instance, due to sudden drop in local pressure. Although extensively studied in isotropic liquids, cavitation in anisotropic liquids has rarely been investigated, and to date, lacks a general framework that can account for the role of long range ordering in cavitation of anisotropic fluids.

Here we present recent experiments on hydrodynamic cavitation in nematic liquid crystal – an anisotropic complex fluid – realized within a microfluidic environment. Cavitation domains, observed under both planar and homeotropic surface anchoring, were created by flowing 5CB, a room-temperature nematic LC, past a micron-sized cylindrical obstacle, placed within a linear microfluidic channel. The cavitation domain, located at the hydrodynamic stagnation point downstream of micron-sized pillar, was created due to the sudden drop in pressure as nematic 5CB flowed between the micron-sized obstacle and the channel walls. The absence of cavitation in similar experiments with 5CB flowing in isotropic phase, suggests that the molecular ordering can potentially lower the cavitation threshold of anisotropic fluids. We confirm the experimental observations using molecular dynamics simulations, and show that the inception of cavitation in an anisotropic liquid is indeed coupled to the global order parameter of the flowing anisotropic matrix.

## Slippery Interfaces -localization and luburication of director rotations

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We have invented the principle and design of slippery interfaces, which has zero anchoring force for attached LC molecules on the interfaces. At first, we succeeded to demonstrate the large reduction of driving voltage in DH-FLC mode of SmC\* keeping the fast switching response. The slippery interfaces can be realized by the spin coated swollen azo-LC gel films on the glass substrates. Under UV irradiation, trans-cis isomerization of the azo-dye co-polymerized in the azo-LC gel film, induces the vertical slippery interfaces by the disordering effect. Since the co-polymerized azo-dye cannot be dissolved into LC, the disordering effect is completely localized in the interface between swollen azo-LC gel and bulk SmC\* material. We greatly improve the reduction of the driving voltage, by lubrication of intra and inter helix C-director rotation motions.

By the lubrication of the C-director rotation by the slippery interface, two types of modes appear in the dynamics of C-director rotation under electric field. Intra helix motion is quite fast, ( $\tau \sim 50 \mu\text{sec}$ ), but it requires rather large driving voltage ( $> 1.5 \text{ V}/\mu\text{m}$ ) and induces small transmitted light intensity ( $\Delta I/I < 0.5$ ). Interhelix motion can be activated by the slippery interfaces, which is rather slow response ( $> 1 \text{ ms}$ ), but easy to be excited by the low driving voltage ( $< 1.0 \text{ V/mm}$ ) and induces the large transmitted light intensity ( $\Delta I/I > 0.75$ ).

Furthermore, we also designed the fast switching & low driving voltage principle with nano slippery interfaces in nematic gels. Confinement effect by the gel network can accelerate the response time of nematic due the localization of director motion as similar way to the cholesteric blue phase. However, the anchoring of the director on the gel network increases the driving voltage. Slippery effect on the nano interface of the gel network can reduce the driving voltage due to the lubrication of the director motion. Since azo dye acrylates are co-polymerized with nematic gels (Azo-NGel), we can demonstrate the UV-switchable nano-slippery interface on the nematic gels.

Dynamic Light Scattering (DLS) provides us the information of the dynamics of director rotation. Dispersion relation of the pure 7CB-T15 mixture completely satisfies the prediction of hydrodynamic modes in the nematic. On the contrary, the relaxation frequency is kept high response in the low wave-number region due to the confinement effect. Electro-Optic response (EO) of the Azo-NGel without UV illumination shows the serious increase of the driving voltage compared to the pure 7CB-T15 mixture. When the Azo-NGel is illuminated by UV-light slippery interfaces can be created by the trans-cis isomerization of the Azo dye of the side-chain on the nano network of nematic gels. EO under UV illumination shows the drastic reduction of the driving voltage keeping the fast response time. We have also confirmed that the dispersion relation of the UV illuminated Azo-NGel is almost the same as that of Azo-NGel without UV illumination by the DLS measurement. Thus, the confinement effect is still effective after the slippery interface is created by the UV illumination.



# A Landau-de Gennes theory for hard colloidal rods: defects and tactoids

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We construct a phenomenological Landau-de Gennes theory for hard colloidal rods by performing an order parameter expansion of the chemical-potential dependent grand potential [1]. By fitting the coefficients to known results of Onsager theory, we are not only able to describe the isotropic-nematic phase transition as function of density, including the well-known density jump, but also the isotropic-nematic planar interface. Due to the enormous reduction of computational effort, we could apply the resulting theory in calculations of non-trivial geometries. In particular, we applied this theory to calculate the isotropic core size in a radial hedgehog defect, the density dependence of linear defects of hard rods in square confinement, and the formation of a nematic droplet in an isotropic background.

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## Large electrocaloric effect in smectic liquid crystals

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Materials with large electrocaloric effect have the promise of realizing solid state refrigeration which is more efficient and environmentally friendly compared to current techniques [1]. A review of recent direct measurements of the large electrocaloric effect in smectic liquid crystalline materials will be given [2,3]. In liquid crystalline materials and mixtures of liquid crystals with functionalized nanoparticles the electrocaloric effect exceeding 8 K was found in the vicinity of the isotropic to smectic phase transition. It is shown that addition of nanoparticles to the liquid crystal host can greatly enhance the operational temperature range and significantly reduce the Joule heating. Liquid crystal materials can thus play an important role as active cooling elements and parts of thermal diodes or regeneration material in development of new cooling devices.

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# Stabilization of topological defects on micro-helices and ribbed colloids in nematic liquid crystal

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When a small colloidal particle is introduced in a nematic liquid crystal, the surface of the particle interacts with liquid crystalline molecules and forces them to align with a preferred direction relative to the surface. This results in the formation of topological defects [1].

Here we study the creation and stabilization of an odd number of topological defects on small colloidal particles which are topologically equivalent to a sphere or fibers of genus  $g=0$ . Oppositely charged pairs of topological monopoles are created by applying a laser-induced local temperature quench. Individually, these monopoles are inherently stable, but since they are paired and oppositely charged, they tend to attract each other and annihilate when their separation becomes less than  $< 40 \mu\text{m}$ . To stabilize the defect monopoles, a gigantic particle is needed [2, 3]. Micro-helices and micro-ribbed-fibres are suitable colloidal particles for the stabilization of topological monopoles with micro-meter separation. The features on the particles stabilize the defects and prevent them from moving toward each other. Further, by controlling the number of and space between ribs on the ribbed-cylinders, any odd number of topological defects with precise spatial positions can be created and stabilized.

The most challenging part of the work is to determine the position and the sign of the large numbers of the topological defects on helices and ribbed-fibres. The sign of topological charges can be defined by probing the elastic deformation field around the particle. To this end, the micro-structures are observed under a polarizing optical microscope, a  $\lambda$  wave-plate is inserted at 45 degrees with respect to polarizer and crossed analyser. The observed birefringence colours enable one to visualize the director field in the vicinity of the defects and micro-structures. The sign of topological charges around micro-structures is also determined using small dipolar colloidal particles. By convention the colloid is assigned a +1 charge and the accompanying point defect is assigned a -1 charge. Such a particle induces an elastic distortion that repels the equally charged part of an elastic dipole and attracts the oppositely charged one.

In addition, we analyse the interaction of the ribbed-cylinders with an arbitrary number of topological charges. This interaction can be explained using a simple topological rule: equally charged parts repel each other and oppositely charged parts attract each other.

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## Large elastocaloric effect in main-chain liquid crystal elastomers

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The elastocaloric effect (eCE) is the mechanical analogue of the number of caloric effects such as magnetocaloric, electrocaloric and barocaloric effect, which can be used in new environmentally friendly cooling technologies. In 2014 the U.S. Department of Energy chooses eC technology as the “Most Promising” among alternatives to vapor compression technologies [1]. The first prototype of regenerative eC heat pump with a temperature span of 15.3 K on the water side, in which eCE is closely related to martensitic transformation of Ni-Ti sheets, was built [2]. However in measured liquid crystal elastomers (LCE) magnitude of the eC responsivity is  $\approx 4\text{KMPa}^{-1}$  and is two orders of magnitude larger than the average eC responsivity of  $\approx 0.04\text{KMPa}^{-1}$  found in the best shape memory alloys [4].

The eCE in LCE is expected to be a consequence of coupling between an external applied stress and the order parameter via the polymeric network. In adiabatic conditions the change in the entropy of the nematic system is compensated by the change of the thermal entropy (adiabatic temperature change).

Results of direct measurements of the eCE in side-chain and main-chain (MC) LCEs will be presented. Measurements were performed on setup, where strain is measured by precision gram sensor while stretching of the sample is controlled with precise translator. Temperature of the sample was measured with thermistor attached to the sample. Measurements of the eC temperature change of LCEs at the constant temperature in the vicinity of the I-N phase transition as a function of the external stress field. The eC change of temperature of 1 K was observed in MCLCEs. An adiabatically applied stress field results in an increase of the material temperature, while the adiabatic removal of stress field results in decrease of the LCE temperature. In both cases total entropy of the whole system remains constant. Taking into account that in MCLCEs strains of 400–600% can be achieved [3] and that relatively weak dependence of the eC responsivity  $\Delta T_{\text{eC}}/\Delta\sigma$  on the strain were observed [4], it is plausible to expect an eC response of several degrees in these materials.

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## Oriented gold nanorods and gold nanorod chains within smectic liquid crystal topological defects

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We show that the use of oriented linear arrays of smectic A defects, the so-called oily streaks, enables the orientation of gold nanorods (GNRs) for a large range of diameters, ranging from 7 to 48 nm, and for various ligands. Moreover, for the small GNRs it enables oriented end-to-end small chains of GNRs when the density is increased from around 2 GNRs/ $\mu\text{m}^2$  to around 6 GNRs/ $\mu\text{m}^2$ . We have characterized the orientation of single GNRs by spectrophotometry and Two-Photon Luminescence (TPL). A strongly anisotropic absorption of the composites and an on-off switching of GNR luminescence, both controlled by incident light polarization is observed revealing an orientation of the GNRs mostly parallel to the oily streaks. A more favorable trapping of GNRs by smectic dislocations with respect to ribbon-like defects is thus demonstrated. The dislocations being localized at a specific localization, the summit of rotating grain boundaries.

Combining plasmonic absorption measurements, TPL measurements and simulation of the plasmonic absorption, we show that the end-to-end GNR chains are either dimers, trimers or quadrimers, all parallel to each other, with a small gap between the coupled GNRs, of the order of 1-2 nm, thus associated with a large red-shift of 110 nm of the longitudinal plasmonic mode. A motion of the GNRs along the dislocations appears as a necessary ingredient for the formation of end-to-end GNR chains, the gap value being driven by the balance between the attracting Van der Waals interactions and the steric repulsion between the GNRs and leading to interdigitation of the neighboring ligands. We thus obtained electromagnetic coupling of nanorods, demonstrate it through light polarization [1].

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## Magnetic domains in ferromagnetic nematic and chiral nematic liquid crystals

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In suspensions of magnetic nanoplatelets in nematic liquid crystals (NLCs), ferromagnetic ordering of the platelets appears which makes the suspensions sensitive also to small magnetic fields [1]. These suspensions can be described macroscopically by two coupled order parameters: the director, which describes the nematic orientational order, and the magnetization. The coupling between the order parameters is such that parallel orientation is energetically most favourable. The director is sensitive to the electric field, while the magnetization is sensitive to small magnetic fields. Similarly, magnetic ordering appears in suspensions of magnetic nanoplatelets in chiral NLCs. However, in this case, the director configuration is preferably helical, while the magnetization favours homogeneous state. As the coupling is such that parallel orientation of the order parameters is most favourable, the system is frustrated.

Magnetic field induces the growth of magnetic domains, which is in both systems dominated by nematic mediated elastic interaction. In a ferromagnetic NLC confined to a layer the domains grow in circular regions, coarsen and after a few field cycles a monodomain sample is obtained. In the chiral case the situation is different. When the ferromagnetic chiral NLC is in a wound helical state, the domain growth is suppressed. The behaviour changes, when a combination of electric and magnetic field is used. For example, we used electric field to unwind the helical structure and a small magnetic field applied in the plane of the layer, i.e., perpendicularly to the electric field, to induce growth of magnetic domains. In this case two types of the domains grew in the form of stripes along the magnetic field, which are seen by polarizing optical microscopy as bright lines. If magnetic field was tilted out of the plane of the layer by a small angle, the response of the stripes was not homogeneous, but brighter and darker regions appeared periodically along the lines. Initially, in the centre of the bright regions of one type of the domains the evolution of defect like structures was observed, and with time also in the other type of the domains similar localized structural changes developed.

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## Dynamics of ferromagnetic liquid crystals

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Experimental realization of ferromagnetic ferrofluids has been a long standing challenge which was only recently overcome by the achievement of stable ferromagnetic order in self-assembled suspensions of magnetic platelets in nematic liquid crystal [1]. These systems combine the orientational order and anisotropic properties of liquid crystals with the physical properties of the colloidal nanoparticles. The orientational order of the nematic induces, through quadrupolar elastic interactions, orientational order on the colloidal particles in such a way that ferromagnetic arrangement of the platelets is favored by magnetic interaction. The resulting macroscopic magnetization  $\mathbf{M}$  lies along the nematic director and is coupled to the nematic director.

Such ferromagnetic coupling between the magnetic field and the optical response allows for field-control of the material properties and opens up the possibility to experimentally study a completely new set of exciting fundamental physical phenomena. For example, they exhibit converse magneto-electric effect, where the electric field induced distortion of the director leads to a distortion of  $\mathbf{M}$  and magneto-optic effects with critical fields two orders of magnitude lower than in pure nematic liquid crystals [2]. In this contribution we discuss the dynamic coupling parameters between the magnetization and the nematic director studied by optical methods. In addition we explore the effect of such coupling on the fundamental orientational fluctuations, whose amplitude and relaxation rates directly depend on the viscoelastic properties. Dynamic light scattering experiments are performed with this purpose at different applied magnetic fields.

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## The impact of local interactions on the formation of smectic mesophases and cybotactic domain formation within nematics

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The simple view of thermotropic liquid crystals points to the presence of two fundamental phases: nematic and smectic. However, within these two structural forms, many subcategories exist. Even within groups of “simple” calamitic and bent-core mesogens, a wide range of smectics are possible; and there are many recent suggestions for new nematic phases. These include the twist-bend nematic phase [1], where the nematic director both twists and bends to produce a helical structure, and the cybotactic nematic phase [2], where it is suggested that nematic order arises from multiple semi-aligned smectic-like clusters.

To better understand what factors contribute to these phases, we use a dissipative particle dynamics (DPD) simulation model, which captures local interactions. This allows for effects, such as anti-parallel association, which occurs naturally in a number of mesogens with terminal dipoles such as the 4-*n*-alkyl-4'-cyanobiphenyl (*n*CB) series; and for other local interactions that could give rise to different forms of cybotactic order.

In large scale simulation studies (~400000 sites) we are able to demonstrate a wide range of smectic phases, including SmA<sub>1</sub>, SmA<sub>d</sub> (smectic phases with non-integer layer spacing) and SmA<sub>2</sub> (bilayer smectic) phases [3]. Within nematic phases, we are able to demonstrate three separate types of cybotactic domains corresponding to normal SmA<sub>1</sub> regions, SmA regions with molecules showing strong antiparallel correlation and ferroelectric smectic regions.

We investigate also the phases that arise from bent-core systems, in which the local interactions change both the nature of the cybotactic domains and the structure of the phases that form.

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During cell division a lens-shaped structure called a spindle is assembled out of cytoskeletal polymers (called microtubules) and various proteins [1]. A similar structure, called tactoid, is observed at the isotropic to nematic transition in a lyotropic liquid crystal, where spindle-shaped nematic droplets form inside the isotropic phase[2]. Inspired by these two examples we set out to investigate the organization of a liquid crystal composed of filamentous *fd*-viruses confined in quasi 2d spindle-shaped microchambers. In addition to the predicted structures [3], the experiments reveal the existence of additional configurations that either feature dislocated defects or multiple nematic domains. Using Monte Carlo simulations, we show that these additional configurations are meta-stable states, appearing on three distinct equilibration pathways. The observed patterns depend on the width of the container as well as on its aspect ratio. The simulations results are in good agreement with the experimental data.

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## Chiral columns from achiral chromonic mesogens and the formation of a new layered chromonic phase

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Chromonic mesophases are a fascinating, but unconventional, form of lyotropic mesophase. Disc-like chromonic mesogens self-assemble in water to form long columns, which at high concentrations self-organise to form lyotropic phases.

Results are presented from simulation models of a series of related disc-like chromonic mesogens [1-2], which demonstrate the formation of novel complex supramolecular aggregates, composed of chromonic columns with dimer and trimer cross-sections. At high concentrations, these aggregates form chromonic N and M phases and, in the case of a “Janus mesogen” (formed from a chromonic disk with three hydrophilic chains on one side of the molecule and three hydrophobic–lipophobic chains on the other side of the molecule), form a novel smectic chromonic phase not previously seen experimentally or theoretically.

In chromonic columns composed of “trimer stacks” (i.e. with a cross-section composed of three-molecules), it is found that achiral molecular aggregates develop a spontaneous twist, inducing the formation of either left-handed or right-handed chiral structures. Chiral aggregates are found to be dynamic entities in which spontaneous chirality inversion can take place over long periods of time.

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## Direct observation of microscopic molecular dynamics in liquid crystal 8CB: Intralayer liquid-like dynamics and interlayer non-liquid-like dynamics

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Gamma-ray quasi-elastic scattering (GQS) method enables us to study the microscopic dynamics (from 0.1 to few nm) at time scales between several nanoseconds to sub-microsecond. The measurable time and spatial scales of the dynamics are quite unique, because highly monochromatized 14.4-keV gamma-rays with a narrow energy-width of 4.66 neV emitted by <sup>57</sup>Fe nuclei excited by synchrotron radiation are used in this method. Generally, a spatial scale of the observed dynamics can be specified by using quasi-elastic scattering method by selecting the detection angle (momentum transfer:  $q$ ) of the gamma rays scattered by the sample. GQS has been applied to the dynamical study in the  $q$  range between 1.5 and 60 nm<sup>-1</sup>. Because the time scale of microscopic dynamics of many liquid crystals is covered by GQS, GQS can be used to reveal the microscopic dynamical picture of liquid crystals directly.

We studied the molecular dynamics of 4'-n-octyl-4-cyanobiphenyl (8CB) in smectic A (SmA) and nematic (N) phases using GQS in the nuclear resonant scattering beamline of SPring-8 (Japan). The relaxation times of the interlayer molecular motion and the intralayer molecular motion are selectively observed by placing the detectors at the angles related to the two X-ray (gamma-ray) diffraction peaks located at  $q \sim 2.0$  and 15 nm<sup>-1</sup>, which originate from the interlayer and intralayer molecular correlations in SmA phase, respectively. The temperature dependence of the relaxation time obtained at the peak located 15 nm<sup>-1</sup> (related to intralayer molecular correlation) follows the Arrhenius law in SmA and N phases. Moreover, the  $q$  dependence of the relaxation time shows a maximum at around 15 nm<sup>-1</sup> in SmA phase as so-called de Gennes narrowing often observed in normal liquids. Thus, in SmA phase, intralayer molecular dynamics is described as a liquid-like dynamics. However, the interlayer molecular dynamics observed at 2.0 nm<sup>-1</sup> doesn't show these characteristics apparently and concluded to be rather affected by the layered order: The temperature dependence of the relaxation time obtained at 2.0 nm<sup>-1</sup> doesn't follow the simple Arrhenius law in SmA and N phases, and the  $q$  dependence of the relaxation time doesn't show an apparent maximum at around 2.0 nm<sup>-1</sup> in SmA phase. This result suggests that the intralayer molecular dynamics is affected by short-range intermolecular interaction as normal liquids, however interlayer molecular dynamics is rather affected by the other parameter such as the smectic layer order.

Thus, we found the clear difference in the mechanism of the interlayer and intralayer molecular dynamics in SmA phase. We further discuss the obtained microscopic dynamical picture of 8CB considering other previously obtained experimental and simulation results.

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Nematic liquid crystals are anisotropic fluids characterized by a long range orientational order. Nematics have the characteristic feature of being elastically responsive to external stimuli such as anchoring constraints of colloidal surfaces. Liquid crystal textures can be considered as an example of topologically complex fields. In general, nematic textures can be identified by a smoothly varying nematic field and localized regions in the shape of points or lines, known as topological defects. By choosing appropriate geometric shapes for colloidal particles and imposing different anchoring conditions on colloidal surfaces variety of topological defects can be formed in nematics and in this way controlled anisotropy can be induced in elastic interactions in a nematic colloidal system. We numerically modeled irregular nematic colloids based upon Landau-de Gennes model. We explain to what extent this irregular geometry can imprint its geometric characteristic features into a nematic structure and how much detailed information about the geometric structure of a colloidal surface is conceivable from the bulk nematic texture.

## Optothermal effects in nematic microflows

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Nematic liquid crystals possess long-range orientational order of molecules that can be controlled by geometrical confinement, topological constraints, and external fields. Past works have primarily studied local viscoelastic responses in static director fields and only recently flows of nematic fluids have been characterised in microfluidic environment. In this work, we focus on optical manipulation and thermal gradients in a flowing nematic medium that can tune and reconfigure multistream flow profiles. We demonstrate the creation and manipulation of dynamically stabilized defect loops and nematic domains in homogeneous and chiral nematics that are sensitive to mechanical forces, temperature changes and geometry variations. We believe that laser tweezers guided control over liquid crystal microflows represents a convenient and versatile tool to drive complex fluid dynamics by optothermal effects.

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## Helical induction in nematic liquid crystals by using chiral metal complexes

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Chiral nematic (or cholesteric) liquid crystals, which are easily induced by adding chiral compounds (dopants) into nematic liquid crystals, have attracted wide attention due to the application to optical and display devices. In contrast, the helix-formation mechanism is still unclear. Our research group has examined a metal complex with a rigid  $\Delta$ ,  $\Lambda$  chirality as a chiral dopant and recently found the clear structural correlation between dopants and resulting helical structure in the aid of MD simulations.<sup>[1,2]</sup> However, we assumed that metal complex dopants are uniformly dispersed in the analysis and calculation. The uniform dispersion of dopants has not been experimentally confirmed due to difficulties in analyzing small amounts of dopants. It is still a general and basic question whether dopants are uniformly dispersed or not in binary chiral nematic system.

To investigate the dopant-host interaction in a wide range of dopant concentration, we examined a new red-colored ruthenium complex (Rutrop-1) with  $\Delta$ ,  $\Lambda$  chirality as a dopant.  $\Delta$ - or  $\Lambda$ -Rutrop-1 exhibits a fairly high HTP and good miscibility for three nematic liquid crystals, 4-cyano-4'-pentylbiphenyl (5CB), 4-pentylphenyl-4-methoxybenzoate (PPMB), and *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA). Raman spectroscopy analysis of binary mixtures of Rutrop-1 and nematics using a green laser ( $\lambda = 532$  nm) revealed a signal attributed to the Rutrop-1 dopant even at a low dopant concentration of  $\sim 0.040$  mol% in the nematics. The strong Raman signal of Rutrop-1 compared to common dopants is attributed to resonance Raman effect. Raman measurements of a binary mixture of Rutrop-1 and nematics in a wide dopant concentrations suggest weak dopant-host and dopant-dopant interactions in N\* media.<sup>[3]</sup>

Because Rutrop-1 was found to exhibit a high HTP and miscibility, which are in a trade-off relationship, blue phase (BP) formation was further examined. Blue phases are liquid crystal phases that appear in a temperature range between a chiral nematic and isotropic liquid phases. BP usually has a three-dimensional cubic structure with lattice periods of several hundred nanometers. 5CB samples doped with 3.6 mol%  $\Delta$ -Rutrop-1 exhibited a BP in the range 24.0 to 25.6 °C upon heating, while those doped with 4.0 mol%  $\Delta$ -Ruacac-1 exhibited a BP in the range 23.3 to 24.5 °C on heating. The role of metal complex dopants on the appearance of BP will be also discussed.

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## Observation of chiral structures from achiral micellar lyotropic liquid crystals under capillary confinement

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The appearance of chirality in a system of achiral components gives rise to fundamental questions about mechanisms of chiral symmetry breaking. Recently the emergence of chiral symmetry broken configurations in achiral chromonic liquid crystals confined in cylindrical capillaries was reported, namely the so-called twisted-escaped radial (TER) and twisted planar polar (TPP) configurations [1]. These new examples of chiral symmetry breaking in liquid crystals were attributed to the twist elastic modulus which is known to be unusually small in the case of chromonic liquid crystals [1]. Strong splay and/or bend deformation can energetically escape into twisting which leads to equilibrium helical structures. In a similar way an unusually small saddle-splay modulus gives stabilized chiral configurations [2, 3].

We now report for the first time the experimental observation of similar chiral configurations in the case of a classical, achiral and non-chromonic lyotropic liquid crystal. The disc-shaped micelles formed by *N,N*-dimethyl-*N*-ethyl-hexadecylammoniumbromide in water with 1-decanol as co-surfactant orient homeotropically at the capillary glass walls. The nematic director field of the lyotropic liquid crystal adapts extremely slowly to the confinement of capillary geometry and changes its configuration when a magnetic field is applied. Thus, we were able to observe within one system the non-twisted configurations like the escaped radial (ER) and the planar polar (PP) as well as the twisted analogues, the twisted-escaped radial (TER) as well as a what we suggest non-planar twisted polar (TP) configuration which can be characterized by a double helix of two half unit disclination lines giving both axial and transverse twist. Similarities and differences to the case of chromonic liquid crystals are discussed, in particular we examine the conditions under which chiral symmetry breaking occurs in this standard non-chromonic lyotropic system. Interestingly, it seems that the chiral TER configuration can be stabilized by the presence of point defects.

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# Liquid Crystalline Behavior of Bio-Inspired Polymer-Clay Nano-Composites

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Laponite, is a widely-used synthetic clay. Laponite powders dispersed in water, hydrate and exfoliate, forming a colloidal dispersion consisting of disk-shaped particles with negative charges on the surfaces and positive charges on the rims [1,2]. Due to Coulomb forces the positively-charged particle rims can be attracted by negatively-charged particle surfaces. Therefore, even at low concentrations, Laponite solutions are found to evolve spontaneously from a liquid-like state to an arrested gel or glassy state, depending on the ionic strength [3,4,5]. This aging process is accelerated as higher Laponite concentrations are used, preventing the system from accessing its potential liquid crystalline equilibrium state. Until now there have been few attempts to suppress this aging process systematically. In this work, inspired by the brick-and-mortar structure found in nacre, we demonstrate a facile strategy to successfully prevent aggregation followed by achieving liquid crystals and then nano-composite films with well-ordered structure. By attaching polymer brushes onto Laponite-particle surfaces, we can screen the negative surface charges and reach steric stabilisation. Using evaporating as means to concentrate the particles, we first observe nematic textures in the more concentrated gel phase. When spreading a liquid drop of the sample and letting it dry completely and repeating this process several times, we are able to obtain transparent films with hierarchical layered architecture. We believe that our simple procedure to form such nacre-like polymer-nano-clay films can open avenues for inexpensive production of advanced materials with novel optical properties.

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## Liquid crystal droplet as a magnetically tunable whispering gallery mode laser

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A microdroplet of liquid crystal (LC) in a medium of lower refractive index acts as a microresonator supporting whispering gallery mode (WGM) lasing [1]. Peak wavelengths of such a laser are set by the phase matching condition of light circulating the droplet perimeter. The optical path in the resonator depends on the droplet shape and internal director structure. We show that in a droplet made of ferromagnetic nematic LC [2], where ferromagnetic nanoplatelets are dispersed in a fluorescently dyed nematic LC, the lasing is tunable by external magnetic field [3].

The droplets, made by manual stirring of LC into the glycerol-lecithin matrix, have a radial director structure with a topological defect in the center. External magnetic field causes elastic distortions of the director structure as the magnetic dipoles of the nanoplatelets tend to align with the applied magnetic field. This results in a changed optical path which in turn causes a shift of WGM peak wavelengths. We show that the wavelength shift is on the order of 1 nm / 100 mT and is linear with the applied magnetic field. The wavelength shift direction (to red or blue) depends on the geometry of the experiment.

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## Micro-structured liquid crystal alignment with out-of-plane surface relief gratings

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Patterned alignment configurations for liquid crystals (LCs) are the core of many advanced LCD operation modes and of several non-display LC applications. Micro-scale surface patterns that induce patterned LC alignment can be of chemical or physical nature. Different patterning techniques are used to realize specific orientation of the LC molecules in miniaturized zones, but, the associated fabrication processes are usually quite complicated and the patterns are mostly simple and uniform.

In our recent work we demonstrated that two-photon polymerization-based direct laser writing (TPP-DLW) is a very convenient technique to generate complex nano- and micro-structures for LC alignment [1]. In addition to fabrication of conventional alignment layers deposited onto glass substrates, the TPP-DLW provides also construction of out-of-plane alignment configurations. In these configurations the LC molecules are uniformly aligned via their contact to side-walls of polymer ribbons oriented perpendicular to the glass substrates. The alignment is induced by surface relief gratings that are created on side-walls of the polymer ribbons during the TPP-DLW process due to optical interference between the incident and reflected laser beams [2]. The measured surface anchoring energy on these side-wall structures is in the range of  $10^{-5}$  J/m<sup>2</sup>, which is considerably higher than observed on conventional surface relief grating materials. With the aid of such polymer ribbons the compartmentalized LCs alignment in arbitrary nano/microstructures can be realized.

The above described alignment method was used to fabricate selected micro-patterned LC configurations exhibiting electro-optic or magneto-optic switching behavior. In particular (i) electrically switchable optical diffraction gratings [3], (ii) electrically tunable q-plates for generation of vectorial vortex beams [4] and (iii) magnetically tunable spatial light modulators were assembled and their properties were investigated.

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## Phase diagram of a smectic-nematic liquid crystal elastomer network based on stress - strain measurements

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Liquid crystal elastomers (LCEs) are composed of polymer chains that are crosslinked together via crosslink molecules, with additionally attached mesogen molecules to the polymer chain. The interplay between entropic elasticity of the polymer subsystem and the spontaneous orientational ordering of mesogenic units results in a reversible thermomechanical response [1]. This unique feature has resulted in a rising interest in LCEs, since it renders them exploitable to many different fields of applications, such as actuators, artificial muscles, smart surfaces, microelectromechanical systems (MEMS), and nanoelectromechanical systems (NEMS) [2, 3].

Spontaneous distortions of the specimen shape and soft elasticity, present in nematic LCEs, is altered in smectic LCEs, because layers cannot move easily across the crosslinking points [4]. We demonstrated that the increase of the relative concentration of smectogenic mesogens in LCEs leads to an increase in Young's module and also a shift in the nematic-isotropic phase transition to higher temperatures. Furthermore, increasing crosslinker concentration in smectic LCEs provides for a random network of defects that could destroy the smectic ordering [4]. It is important to note that temperature-resolved stress-strain measurements allow for the determination of the nematic-smectic phase boundary in smectic LCEs, in contrast to thermomechanical measurements, which can only identify the nematic-isotropic phase transition.

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## Density-functional theory of lyotropic nematic order in semiflexible dimers

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The isotropic-nematic phase transition is investigated for a solution of flexible molecules consisting of two rigid rods connected by a spacer with variable bending stiffness. Strictly excluded volume interactions are taken into account in this (athermal) model. A molecular mean field theory is used to determine several order parameters, dictated by the complex symmetry of the system, as functions of the density. The earlier work on lyotropic ordering of rigid bent-rod molecules is reproduced and extended to show the second-order phase transition at the Landau point, in a narrow range of bend angles. For the flexible double-rod molecules, the phase diagram of the system is generated in terms of the variables spacer stiffness and particle number density, with an apparently novel biaxial phase found in spite of a lack of intrinsic molecular biaxiality.

## Active particle filtering by liquid crystal microfluidics

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The control of fluids on a micrometre scale is of great importance in many fields including biotechnology, health care industry, and chemistry. Recently, the use of liquid crystals was introduced [1] in microfluidic chips showing extraordinary properties and superior controllability compared to isotropic fluids. The special properties of liquid crystals arise from their structural anisotropy: the local average of molecular orientation (the so-called director) can be affected by electric/magnetic fields, electric polarization is coupled to director gradients, the director orientation is coupled to flow, and the effective viscosity is orientation dependent. Consequently, liquid crystals offer much more ways of flow control and tuning by external stimuli than common isotropic liquids.

We investigated liquid crystals carrying colloids in microfluidic chips allowing the application of electric field in segments of the channel system. Depending on the use of different frequencies and magnitudes of the electric field, we found two effects: 1) to trap particles by forcing them to be adhered on channel walls even after switching off the voltage, and 2) to remove them allowing the colloids to follow the net flow. We will present the characteristics of threshold voltages for the trapping and the releasing mechanisms. Furthermore, the effects of the net flow speed, channel/electrode geometry, and particle size will also be revealed. We will show that the new effect of active particle filtering is exclusively allowed by the anisotropic nature of liquid crystals and cannot be observed in the case of isotropic fluids.

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Mesophase formation is critical in the formulation of many typical household products. However, phase diagrams of complex surfactant-additive mixtures remain challenging to predict. We apply Dissipative Particle Dynamics (DPD) simulations to this problem in order to equip industry with the tools to better (and more cost-effectively) develop new products.

DPD is a mesoscale simulation method, with the ability to retain molecular detail while simulating at the level of micrometers and milliseconds. A defining feature of DPD is its soft purely repulsive inter-particle interaction. This allows for longer time and lengths scales to be accessed in comparison to conventional simulations. This rather unique characteristic makes DPD the ideal method to investigate mesophase behaviour as it can rapidly map out phase diagrams.

Our study focusses on the parameterization of a highly transferable DPD model that describes the phase behaviours of common anionic surfactants (sodium dodecylsulphate, linear alkylbenzene sulphonates, and alkylether sulphonates) across concentration ranges and in various combinations.

To extend these models to surfactant/polymer/additive mixtures, we are developing methods to automate DPD parameterisation for a series of molecules. With this tool at our disposal, we can rapidly investigate complex mixture phase diagrams, to see how addition of polymer, perfume, and other additives affects commercial surfactant products.

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## Nematodynamics in microcapillary junctions

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Flows of confined nematic fluids are of interest in microfluidics, showing possible applications in optics, sensing, material synthesis, and transport [1], and in the context of multistable memory devices, based on the nematic porous networks [2,3]. In junctions of nematic microchannels, there exists an intricate interplay between singularities in two fields – a stagnation point in the velocity field and topological defects in the orientational field of the nematic order [4]. Here, we investigate nematics in three-dimensional junctions of 6 cylindrical capillaries by means of hybrid lattice-Boltzmann numerical simulations. Equilibrium nematic field in such junctions depends on the orientation of the escaped configuration in individual channels. In a single capillary, flow acts as a driving mechanism which tends to align the nematic director along the capillary. By inducing flow through microjunctions, flow aligning mechanism sets the defect configuration in the junction. Depending on the geometry of the flows in/out of the junction, we observe point defects, configuration without singularities in the bulk, or a set of disclination lines stretching out of the junction. We test different geometries of the induced flows and the dynamics of topological defects in the nematic field as it changes from the equilibrium configuration to a new flow-defined stationary state with different topological characteristics. Finally, this work is a contribution towards understanding defect behavior in nematic microfluidics and porous networks.

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## Chiral Nitroxide Radical Liquid Crystals as Novel Magneto-Optical Soft Materials

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All-organic liquid crystals (LCs) containing a five-membered ring nitroxide radical (NR) moiety in the mesogen core (NR-LCs) have attracted a great deal of attention as one of metal-free novel soft materials because they exhibit unique properties potentially applicable to next-generation devices [1,2]. For example, NR-LCs have much larger magnetic susceptibility than the classical diamagnetic LCs and they form self-organized photonic band gap (PBG) structures in chiral nematic (N\*) phases. The coupling of these properties would induce strong magneto-optical effects, which holds great promise for the novel magneto-optical devices. However, due to their high melting points, both the fundamental and application researches on the magnetic and magneto-optical properties have made little progress.

Here, we report a new NR-LC showing a low melting point as a practical magneto-optical material; it exhibits an N\* phase at 36 °C and maintains the extremely stable supercooled state to about 0 °C. Its fundamental properties such as phase transition behaviors, optical properties and magnetic properties were studied. In particular, its fluidity facilitates the complicated shape fabrications and its magnetic and optical properties in the N\* phase are interesting; we can prepare microcapsules with a shell consisting of the new NR-LC by utilizing the microfluidic device [3] and ELIXIR method [4], and it shows magnetic-field-driven transportation and temperature-dependent color resulting from its tunable PBG. Of course, it shows an abrupt increase of magnetic susceptibility at the crystalline-to-N\* phase transition (magneto-LC effects) as well as conventional NR-LCs [2].

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# A molecular dynamics study of physical properties of chiral metal complex dopants in nematic liquid crystals

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Some chiral compounds have a great role to induce the macroscopic helical structure in nematic liquid crystals (LCs) and a variety of the compounds have been synthesized [1]. The important characteristics of the chiral dopants as components of chiral nematic LC systems are the helical twisting power (HTP) and solubility in host nematics. Inorganic octahedral metal complexes with a rigid and screw-shaped  $\Delta$ ,  $\Lambda$  chirality have been brought to our attention because of its high helical twisting power [2, 3]. However, metal complex dopants generally have low miscibility in common nematic LCs.

In order to develop novel optical devices utilizing the metal complex doped chiral nematic LC materials, it is required to design the metal complex dopants with the high HTP and good miscibility in host nematic media. Therefore, the aim of our study is to understand the relationship between the molecular structure and the physical properties of the metal complex. We here present a theoretical study to investigate the microscopic structure and dynamics for the binary system of chiral ruthenium dopants and nematic LC molecules by means of all-atom molecular dynamics (MD) simulation.

MD simulations were performed for the racemic system composed of both  $\Delta$ - and  $\Lambda$ -isomers of the chiral ruthenium dopants and surrounding nematic LC molecules [4]. While we cannot represent the enantiomeric system forming the micrometer-scale helix by all-atom MD methods, the racemic system without the helix is the appropriate simulation model for analyzing the static and dynamic properties from the microscopic point of view.

The helical twisting power per dopant molecule (denoted as  $\beta_M$ ) can be estimated based on the surface chirality model proposed by Ferrarini *et al.* [5] and simply expressed as the product of the helicity tensor  $Q$  and the ordering matrix  $S$ .  $Q$  can be calculated from the molecular structure, whereas we can obtain  $S$  from MD simulation results. As a result, the  $\beta_M$  values of several types of ruthenium dopants obtained in this study show good correspondence with those measured in the experimental studies.

We also analyzed the means square displacements and the diffusion coefficients for the metal complex dopant molecules and the nematic LC molecules. The results indicate that the diffusion behavior of the molecules in the system depended on the miscibility of the chiral dopant. It also gives new insight into designing a chiral metal complex dopant with better miscibility in the nematic LCs.

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# Nanosecond optical imaging of phase transitions dynamics in liquid crystals

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Continuous symmetry breaking phase transition have been extensively studied in a large variety of physical systems including condensed matter, Universe and liquid crystals [1-3]. Non-equilibrium symmetry breaking is well described using the Kibble – Zurek mechanism, which describes the formation and structure of defects and domains as a function of the rate at which the symmetry was broken [4, 5].

In our experimental study we aim at observing the formation of the domain structure in a nematic liquid crystal after a sudden temperature drop throughout the isotropic-nematic phase transition. The main experimental problem to be solved is imaging of instantaneous pattern of defect tangle within the nanosecond time interval. We set up an experimental set up around a picosecond laser illumination system, which allows us to achieve incoherent light exposure times of 20 ns. The sample was locally heated using another laser, which allows us to achieve fast cooling rates of the order of 10 K/millisecond. We are able to capture photographs of dynamic nematic defects patterns by using optical polarization microscopy and a high sensitivity and high resolution camera at 20 ns.

We use numerical modelling to calculate the thermal properties of the system we study i.e. the inhomogeneous initial temperature field and the local cooling rate caused by the Gaussian shape of the heating laser beam. We observe dynamics of formation of the nematic ordering at the isotropic nematic interface where the temperature drop is the smallest and also nucleation sites are present. The ordering interface moves towards the centre of the heating area, speeding up towards the centre due to the increase of the cooling rate. Behind the interface we see the formation of domains where their size increases depending on the local cooling rate and of the time after the system locally cools below the phase transition temperature. We show that it is possible to image the onset of early time regime, which is beyond the Zurek time for this system.

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## The Induction of the Ntb Phase in Mixtures of non-Ntb Forming Cyanobiphenyl Dimers

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The uniaxial apolar Nematic phase (N) is the simplest and most widely known liquid crystal phase, where the molecules possess only short-range orientational order. When the molecules are chiral they pack in nematic-like layers, where the director twists in a helical structure, forming the chiral nematic phase (N\*). The recently discovered Ntb mesophase [1,2], below the high-temperature N, has been argued to represent the link between N and the N\* phases. This new phase exhibits nematic features, according to X-ray studies, and smectic optical textures under the microscope [3]. However, the most striking characteristic is its spontaneous chirality, even though the Ntb is formed by achiral odd-membered dimers [1–3]. Despite a tremendous amount of work, both experimental [4,5] and theoretical [6,7], the structure-properties relationships defining the occurrence of the mesophase are not yet fully understood. Nevertheless, the general notion is that the phase formation results from chiral conformers leading to the spontaneous breaking of the chiral symmetry.

Within this framework we make a contribution to the understanding of this mesophase by reporting for the first time the induction of the Ntb phase in a series of mixtures between cyanobiphenyl dimers which on their own are only nematogenic. The mesophase behaviour of the systems under study, the stability and the concentration/temperature range of the Ntb phase will be presented, combining Polarizing Optical Microscopy, Differential Scanning Calorimetry and X-ray Diffraction results and an interpretation of the occurring Ntb phase will be discussed.

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## Dielectric anisotropy studies of CBnCB/5CB and CBnCB/CBOnOCB mixtures exhibiting two nematic phases

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The recent discovery of a novel nematic phase, termed as nematic Nx or twist-bend nematic (Ntb), has attracted remarkable scientific interest over the last few years due to its fascinating features [1-6]. This new mesophase, initially observed in odd membered methylene linked liquid crystal dimers upon cooling from the conventional nematic phase, is characterised by spontaneous twist of a phase axis and does not exhibit long positional order. Nx/tb phase is chiral in nature although consisting of achiral mesogens, which is thought to be a major breakthrough in soft matter and materials science in general [1, 2]. The structure and physical properties of the Nx/tb phase have been probed via several complimentary characterisation techniques [3, 4]. Furthermore, the occurrence and the stability of the Nx/tb phase have been tested in mixtures [5, 6]. However, its structure-properties relationships are still under debate.

In this work we investigate the dielectric response of binary mixtures of symmetrical odd membered cyanobiphenyl methylene-linked dimers either with their corresponding monomeric compound or with their ether-linked analogues. The static dielectric response and dielectric anisotropy of neat materials and mixtures are probed by means of Broadband Dielectric Spectroscopy (BDS). The alignment of the samples is confirmed in treated cells with and without the application of an external electric field, under the microscope. In addition, miscibility and mesomorphic behaviour of the mixtures are studied by means of Polarizing Optical Microscopy (POM). The results are to be discussed in connection to key molecular features (shape, flexibility, position of dipoles etc.) of the dominant conformations adopted by the molecules. Comparison of the results of the neat materials with the ones obtained in the cases of mixtures are expected to give deeper insight into the self-organisation of the constituent molecules within the mixtures.

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## Particle diffusion in ferromagnetic liquid crystals

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We experimentally studied diffusion of microparticles in liquid crystals. Spherical micron-sized particles were immersed into liquid crystals and their motion was observed through an optical microscope. Separate diffusion coefficients were determined, depending on the direction of motion relative to the orientation of the director. Apart from the standard nematic liquid crystal (E7) also recently discovered ferromagnetic liquid crystals were investigated. In these materials, magnetic platelets are introduced into the nematic forming a stable ferromagnetic suspension. Such systems are very sensitive even to low external magnetic fields, leading to a strong magneto-optical response. Fields as low as 10 mT suffice to reorient the magnetic moments coupled with the liquid crystalline ordering, while simultaneously enhancing the long range director fluctuations.

We studied particle diffusion in the presence of an external magnetic field for reduced as well as for increased fluctuations. While the dynamics in E7 is too fast for observing anomalous diffusion, we see sub-diffusion and a general decrease in the diffusion coefficients in the ferromagnetic samples. Since no significant dependence of the diffusion on the external field is observed, we conclude that the sub-diffusion in the ferronematic liquid crystals is a consequence of local heterogeneities.

## Molecular Dynamics in a “de Vries” Liquid Crystal: <sup>1</sup>H NMR Relaxometric Study

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Liquid crystals that exhibit de Vries smectic A phases are promising materials for new generations of ferroelectric liquid crystal displays and other electro-optical devices.

Here we present a detailed study of molecular dynamics by means of proton NMR spin–lattice relaxation in a (S)-hexyl lactate derivative, 9HL liquid crystal. 9HL exhibits a de Vries SmA phase over a broad temperature range. The proton relaxation data was obtained over the whole temperature stability range of SmA and SmC\* phases for a few selected frequencies. In addition, proton relaxation was measured as a function of Larmor frequency from 5 kHz to 100 MHz for a few selected temperatures. The relaxation data was consistently analyzed using relaxation models for translational self-diffusion (**D**), rotations/reorientations (**R**), layer undulations (**LU**), and tilt director fluctuations (**TDF**). Close to the SmA–Iso phase transition temperature, the relaxation dispersion is very similar to that observed for regular/conventional SmA phases. However, on the cooling, the relaxation dispersion strongly deviates from the usual sum of SD, R, and LU contributions, and an additional relaxation mechanism had to be considered. This mechanism could not be consistently assigned to individual azimuthal reorientations of the molecules that would be anticipated in the random diffuse cone model. The other models, namely the conformational and interdigitated models, are not sufficient to explain the appearance of tilt fluctuations. Moreover, the temperature dependence of the relevant parameters across the SmA–SmC\* phase transition strongly supports the appearance of cluster of tilted molecules in the SmA phase close to the transition. In fact, molecular dynamics interpreted in terms of SD, R, LU, and TDF mechanisms is the most consistent with the phase structure proposed by the cluster diffuse cone model.

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In this work, using a hybrid Lattice Boltzmann algorithm [1], we numerically study the switching dynamics of 2D cholesteric emulsions immersed in an isotropic fluid under an electric field, either uniform or rotating with constant speed. The overall dynamics mainly depends on the magnitude and on the direction (respect to the cholesteric axis) of the applied field, on the anchoring of the director at the droplet surface and on the elasticity [2, 3, 4]. If the surface anchoring is homeotropic and a uniform field is parallel to the cholesteric axis, the director undergoes deep elastic deformations and the droplet typically gets stuck into metastable states rich in topological defects. When the surface anchoring is tangential, the effects due to the electric field are overall less dramatic, as a small number of topological defects form at equilibrium. The application of the field perpendicular to the cholesteric axis usually has negligible effects on the defect dynamics. The presence of a non-uniform rotating electric field of varying frequency fosters the rotation of the defects and of the droplet as well, typically at lower speed than that of the field, due to the inertia of the liquid crystal. If the surface anchoring is homeotropic a periodic motion is found. In the past isotropic droplets in a nematic solvent [5], liquid crystal blue phases under electric fields had been investigated [6, 7, 8] and equilibrium defect structures in cholesteric liquid crystal droplets were known [9].

Our results represent a first step to understand the dynamical response of a cholesteric droplet under an electric field and its possible application in designing novel liquid crystal-based devices.

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## Localization of low-molecular-weight molecules at the defect of a liquid crystal

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Topological defects in liquid crystal have intrigued scientists because most of them are readily observed by optical means. Moreover, they have been drawing greater attention also as a means of manipulating and arranging macroscopic objects such as colloidal particles; topological defects have been known to trap such objects. The mechanism of this trapping is rather simple; trapped objects at the topological defects reduce the total free energy of the system by replacing the energetically costly regions at the cores of the defects.

However, it remains unclear whether the same mechanism can work for small molecules that do not self-assemble in the bulk of the liquid crystal. In contrast to macroscopic objects, the behavior of small molecules is dominated by entropy which yields their uniform distribution unless phase separation or self-assembly is driven by enthalpy.

Here we show, both experimentally[1] and theoretically [1, 2], that the trapping power of topological defects can be strong enough to give rise to a non-uniform distribution of such non-liquid-crystalline small molecules (guest molecules). Experiments using fluorescent molecules clearly demonstrate the assemble of the guest molecules at topological defects resulting in their gleaming[1]. Our theoretical analysis[2], based on the combination of the Flory-like theory for mixing and the Landau-de Gennes theory for the evaluation of the defect core energy, allows quantitative evaluation of the excess of the guest molecules at the defect core. Tailored arrays of topological defects could therefore be utilized as a scaffold for the assembly of small molecules providing novel structures and functions, and we hope that our work will motivate further experimental studies towards the design of novel functional materials making use of topological defects.

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## Hydrodynamic cavitation in Stokes flow of anisotropic fluids: Simulations and Theory

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The cavitation of liquids under tension is ubiquitous in fluid dynamics, and has significant, and often deleterious, effects on a wide range of industrial and biomedical applications. Although extensively studied in isotropic liquids, investigations in anisotropic fluids are scarce, and till date, no systematic attempt has been made to study them. Here we report nonequilibrium molecular dynamics (MD) simulations of a nematic liquid crystal that exhibit cavitation due to a sudden drop in pressure upon flow past a micron-sized obstacle in microchannels. We study the physical principles governing the cavitation phenomena in nematic liquid crystals, and identify a critical value of  $Re_{cr}$  for cavitation inception that scales inversely with the characteristic order parameter of the anisotropic fluid. Strikingly, the  $Re_{cr}$  for nematic fluids can be as low as about 50% of the cavitation threshold in isotropic fluids. The inception, followed by growth of the cavitation domain, ensues in the Stokes flow regime. We also develop a theory that correctly predicts the decrease of the  $Re_{cr}$  as the nematic order increases. Corresponding microfluidic experiments on 5CB are in agreement with the theory.

## Molecular simulations elucidate soft elasticity in polydomain liquid crystal elastomers

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Liquid crystal elastomers (LCE) — polymer networks with embedded liquid crystal units — are functional materials characterized by a pronounced coupling between elastic strain and liquid crystalline orientational ordering. When prepared by polymerization and cross-linking in the isotropic phase, and then cooled, the resulting polydomain materials exhibit an extraordinary soft elastic behavior under unidirectional pulling, with a plateau-like region in the stress-strain curve, before turning into a monodomain LCE where a standard elastic resistance is recovered [1, 2]. Here we investigate the microscopic origin of this behavior [3] by performing large-scale molecular iso-stress Monte Carlo simulations of swollen polydomain main-chain LCE. Our simulations are based on the soft-core Gay-Berne interaction potential [4] and reproduce the stress-strain experiment featuring the plateau-like behavior. Deeper insight into the molecular organization of our simulated samples reveals that the underlying mechanisms are local domain rotation and growth, excluding orientational order destruction-reconstruction. It also suggests that these mechanisms may be assisted by a dissipation of elastic free energy stored in topological defects created during the synthesis, which is compatible with the stress-strain irreversibility observed in some main-chain LCE.

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## Spontaneous breaking of chiral symmetry due to octupolar (tetrahedral) order

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In systems with internal structure (internal order) chiral symmetry is broken, if the spatially inverted structure is different from the original one and cannot be made congruent to it by simple rotations. Such systems are called chiral or it is said they possess handedness. Broken chiral symmetry includes broken inversion symmetry, but the inverse statement is not true. *E.g.*, polar order (the existence of a polar vector or polar direction) breaks inversion symmetry, but not necessarily chiral symmetry. The hallmark of broken chiral symmetry is the existence of a pseudoscalar quantity, a scalar that changes sign under inversion. The symmetry breaking is called spontaneous, since the free energy of the system is a true scalar quantity.

Very well-known examples of chiral phases are cholesteric and smectic C\* liquid crystals, where chiral molecules give rise to a helical ground state of the nematic direction. The pitch of the helix is a pseudoscalar. A different type of chirality occurs for (achiral) bent-core (banana) molecules, where at least one preferred direction is polar (rather than nematic). Embedded within smectic layers and tilted w.r.t. the layer normal, chiral phases occur [1, 2], CB2 and CG of  $C_2$  and  $C_1$  symmetry, respectively. Their chirality is called ambidextrous, since it is of geometrical origin and there are two energetically equivalent structures that are chiral images of each other. They are characterized by pseudoscalars of opposite sign. Similar ambidextrous chirality occurs in columnar phases [3, 4].

Here we will discuss chiral symmetry breaking due to the existence of octupolar (tetrahedral) order. The latter is characterized by four unit vectors defining a tetrahedron, and is described by a fully symmetric rank-3 tensor order parameter. It breaks inversion symmetry and leads to the optically isotropic  $T_d$  symmetric phase. When combined with nematic order one can get ambidextrous helicity and ambidextrous chirality [5, 6]. The former case arises in a  $D_{2d}$  symmetric phase, where the nematic direction is along one of the (improper) 4-fold tetrahedral axes. Although there is no chirality in such a phase, the ground state is helical (combined rotation of the nematic and the tetrahedral directions) with both helical senses energetically equivalent. The origin is an achiral linear gradient term in the free energy. If the uniaxial nematic is replaced by an orthorhombic biaxial one, a  $D_2$  symmetric phase arises, which is chiral and not only shows ambidextrous helicity, but also ambidextrous chirality. When octupolar order is present in an isotropic transient elastic (viscoelastic) medium, ambidextrous helical domains can occur [7].

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## Colloidal liquid crystals in confinement: isotropic, nematic and smectic phases

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The interest in confinement of liquid crystal phases arises from the rich interplay between packing problems related to local boundary conditions and the competing elasticities and defects. The focus, however, has largely been on the confinement of the nematic phase, certainly from an experimental point of view. Here we present recent results on the confinement of colloidal silica rods in three dimensional chambers with two dimensional geometrical footprints [1]. Exploiting the rods' relatively large density difference with respect to the dispersing solvent, we observe coexistence of isotropic liquid, nematic and smectic phases.

The rods are synthesized following the method of *Kuijk et al.* [2]. Using confocal microscopy and soft lithography techniques we characterise the liquid crystalline structures at the single particle level in chambers with sizes ranging from three to forty rod lengths. We observe smectic bridge structures in square cavities, which is in good agreement with simulations [3]. The structures observed in other confinement geometries are discussed and compared with theory. Finally, we highlight the interplay between the coexisting nematic and smectic phases in confinement, and discuss how this may lead to the determination of the twist elastic constant for colloidal rods.

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## Characterization of the thermotropic phase behavior and microscopic structure of a confined discotic liquid crystal

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Discotic liquid crystals (DLC) filled into cylindrical nanopores exhibit a liquid crystalline phase with their molecules arranged in hexagonal columns. The columns orient perpendicular (radially) or parallel (axially) with respect to the pore axis depending on surface anchoring conditions and pore size. Axially oriented columns enable the fabrication of organic nanowires utilizing the high conductivity in the stacking direction due to overlapping  $\pi$  – electrons. This leads to interesting applications in e.g. organic semiconductor-based devices. The molecular ordering of the liquid crystalline columns can be probed by temperature dependent optical retardation measurements [1, 2] supplemented by X-ray diffraction sensitive to the translational order [3].

We investigated the DLC 2, 3, 6, 7, 10, 11 - hexakis [hexyloxy] triphenylene (HAT6) embedded in nanoporous alumina and silica membranes as function of the pore diameter (12 nm - 180 nm). Due to their hydrophilic nature porous membranes enforce face-on anchoring leading to a radial orientation. To obtain edge-on anchoring conditions, and thus favoring axial orientation, the silica membrane surface is chemically modified. The optical retardation measurements show that the columns orient radially in these membranes independent of the anchoring conditions. Interestingly, a quantized phase transition of each molecular layer is found indicated by a distinct increase of the optical orientation. Additionally, an axial orientation of HAT6 filled into alumina membranes with a pore diameter of 25 nm is achieved. A Landau-de Gennes ansatz semi-quantitatively describes the phase transition behavior observed [2]. X-ray diffraction experiments performed at the 3rd generation synchrotron radiation source PETRA III at DESY giving detailed information about the translational order support these findings. Summarizing, this study shows the existence of a phase transition in the molecular range as well as the suitability of the membrane with 25 nm pores as a template for preparing organic nanowires.

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Liquid crystals confined in closed cavities usually form topological point defects due to the frustration of the director field induced by the surface. A delicate balance between the surface anchoring strength and the elastic energy of the liquid crystal determines the stable director configuration. However, recent simulation work on dense systems of particles in very small cavities [1] (which incur large director distortions), has shown that spatially extended defects may also form.

Here, we study the formation of topological defects in a system of short rods confined to a circular cavity with a radius of a few particle lengths. We analyse two cases: (i) two dimensional hard rods in thermal equilibrium using Monte Carlo simulations, and (ii) experiments on vertically vibrated quasi monolayers of granular rods in steady state. Despite of being fundamentally different, both systems share common features. In bulk, rods with a length-to-width ratio  $\kappa \leq 7.5$  form a tetratic phase characterized by two directors perpendicular to each other (four fold symmetry) [2, 3]. Confinement introduces frustration that results in a distorted director field and the formation of four identical disclinations symmetrically located near the surface. Other characteristics such as the tendency to form clusters and the fluctuations are significantly different in both systems.

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## Percolation theory of aligned polydisperse carbon nanotubes in composite materials

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The design of polymer composites with conducting fillers like carbon nanotubes has a wide range of potential applications in the electronics and photovoltaics industry. Above a critical particle concentration called the percolation threshold, the nanorods start forming a system-spanning network which strongly affects the macroscopic mechanical and transport properties of the material.

The percolation threshold of a polydisperse system has long been known to scale with the inverse weight-average of the particle length distribution. Invoking connectedness percolation theory, we find that this relation does not generally hold anymore in the presence of external alignment fields, such as electric fields, elongational flow fields and molecular fields provided by nematic liquid-crystalline hosts.

## Topological formations in chiral nematic droplets

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Confined chiral nematic liquid crystals are rich in exotic topological structures because of the interplay between the chiral structure and the frustrating confinement. We present new topological structures which form in chiral nematic droplets with homeotropic anchoring: strings of point defects with unit topological charge, polyvalent point defects with  $q = -2$  and  $q = -3$  topological charge and structurally complex topological molecules.

To study the complex 3D structures in the droplets we developed an extension of fluorescent confocal polarising microscopy (FCPM) [1], which uses a simulated annealing algorithm to fully characterise the local orientation of the LC director field [2]. The extended method enables us to visualise the complex 3D structure of the droplets, revealing that strings of charge-alternating point defect can be stabilised by cholesteric bubbles, which are localised toron-like chiral structures. These cholesteric bubbles can, because of the high symmetry of the spherical confinement, also stabilise defects which have not been observed before - the triangular  $q = -2$  and the tetrahedral  $q = -3$  higher-charge point defect which bind with a suitable number of  $+1$  defects to compensate the total charge of a droplet to 1. This higher valence of the defects enables the formation of complex topological molecules in which one of the point defects with unit charge is replaced by a complex formation of several point defects with equivalent total topological charge [3].

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## Dislocations in blue phases

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Disclinations in blue phase I and blue phase II exhibit a regular cubic lattice structure analogous to atomic arrangement in crystals. As a result, dislocations, which are conventionally found in crystalline solids, are also expected to exist in blue phase disclination networks. In this work, we employ finite difference relaxation method to simulate both edge and screw dislocations in blue phases. By calculating and visualizing the order parameter field in the regions of dislocations, several possible structures are predicted. Dislocations with lowest strengths (smallest Burgers vectors) are found to be energetically favorable, same is the case with dislocations in crystalline solids.

## Development of coarse grained models for chromonic liquid crystals

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The simulation of chromonic liquid crystal phases is often challenging for a number of reasons. While atomistic models are often useful for small systems (ie. a single chromonic stack), modelling an entire phase would be prohibitively expensive. Coarse grained simulations are necessary for these larger simulations, but standard methods for parametrising coarse grained models are more well suited to isotropic systems.

Past work in our group has involved the modelling of the non-ionic chromonic liquid crystal molecule TP6EO2M at the atomistic [1] and highly coarse-grained DPD (dissipative particle dynamics) [2] levels. In this work, we discuss how to parametrise systematic coarse grained models for this system, which are computationally cheaper than the atomistic model, but keep chemical specificity.

We compare results from common *bottom-up* (force matching) and *top-down* (MARTINI and SAFT) coarse graining methods, and show that the *top-down* models are able to qualitatively reproduce the stacking structure and thermodynamics of the atomistic system. The performance of these models give us useful insights into how the balance of hydrophobic and hydrophilic interactions leads to the self-assembly of chromonic stacks. We also discuss how the coarse grained models may be improved to achieve more quantitative accuracy.

The methods presented here should be generally applicable to other chromonic liquid crystals. This will allow insight into the behaviour of these systems which was previously inaccessible to simulations.

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## Role of the anchoring energy on the texture of cholesteric droplets: finite element simulations and experiments

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In an unconfined cholesteric domain, the director  $\vec{n}$  rotates around a single space direction by forming the so-called equilibrium cholesteric helix. In a confined domain, such as a cholesteric droplet, the helix is deformed due to the anchoring conditions on the domain boundaries. If the anchoring is sliding on the boundaries, which we assume in this poster, the anchoring potential  $\gamma$  only depends on the angle  $\theta$  between the director and the normal to the surface  $\vec{\nu}$  and passes through a minimum for a preferred angle  $\theta_a$  with  $\gamma(\theta) = W_a(\theta - \theta_a)^2$  at small deviations  $|\theta - \theta_a| \ll 1$ . Angle  $\theta_a$  is called the anchoring angle and  $W_a$  is the anchoring energy.

In this work, we are interested in numerically computing the textures of cholesteric droplets in coexistence with the isotropic phase [1].

In such a case, the anchoring energy is moderately weak, and one can assume that these textures are free of topological defects. Under this assumption, the texture of a cholesteric droplet can be found by minimizing the Frank free energy. We introduce a numerical minimization method, based on a trust region strategy and the truncated conjugate gradient algorithm of Steihaug [2], which has two interesting properties: it always converges to a local minimum of the free energy (contrary to the Newton method of Gartland *et al.* [3] and Adler *et al.* [4]), and the convergence is quadratic in a local neighborhood of the solution (contrary to the gradient descent method of Gil *et al.* [5]).

We apply this algorithm to study the texture of cholesteric droplets in coexistence with their isotropic liquid in two cases: when the anchoring is planar and when it is tilted. In the first case, we show how to determine the anchoring energy at the cholesteric-isotropic interface from a study of the optical properties of droplets of different sizes oriented with an electric field. This method is applied to the case of the liquid crystal CCN-37. In the second case, we come back to the issue of the textural transition as a function of the droplet radius between the double-twist droplets and the banded droplets, observed for instance in cyanobiphenyl liquid crystals. We show that, even if this transition is dominated by the saddle-splay term  $K_4$  as was recently recognized by Yoshioka *et al.* [6], the anchoring energy does also play an important role that cannot be neglected.

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# Isotropic and nematic liquid crystalline phases of 2-state rotaxane switch

3.059

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A rotaxane is a molecule comprised of mechanically interlocked components, as opposed to covalently bonded components. In a typical rotaxane, rings are threaded on a rigid molecular axle with bulky ends to prevent rings from de-threading. Rings are not covalently bonded to the axle and are free to adapt position along the axle. Such a molecule has been synthesised to act as a 2-state molecular switch [1] where relocation of the ring on the axle also changes the molecular length or aspect ratio.

Liquid crystals are solutions of anisotropic molecules which have no long-range positional order, like a liquid, but can have phases which possess different degrees of molecular orientation similar to crystalline ordering. The phases in lyotropic liquid crystals are determined by the concentration of the molecules. Onsager [2] first described isotropic-nematic phase transition of rod-like molecules from fundamental thermodynamic principle. We extend Onsager's theory to system of 2-state rotaxane, where rod length can be altered by an external field [3] as well as being labile and "adapt" to prevailing concentration [4]. We construct phase diagrams and show that by triggering length switching, isotropic-nematic phase transition can be achieved without changing concentration.

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## Waveguiding with liquid crystal director profiles

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Optical birefringence is a fundamental property of liquid crystals, and it defines many of their noteworthy and diverse applications. With controlling the direction of the optical axis in liquid crystals, the flow-of-light of the extraordinarily polarized beam can be manipulated to a high extent.

We will focus on waveguides, filled with liquid crystals entirely. We will demonstrate the numerical simulations of radially polarized light propagating through liquid crystal waveguide with various radially symmetric director profiles. The chosen director profiles are a modification and upgrade of profiles, presented in [1]: a defect disclination line running along the waveguide, with different boundary conditions at the perimeter of the cylindrical waveguide. Spatially changing direction of the optical axis and thus different refractive index profiles lead to stable modes of light beams, which can be found for each profile. The modes resemble Laguerre-Gaussian beams and are additionally characterised with specific tuning between the value of the (positive) anisotropy of refractive index and the waist width of the incoming beam. In some cases, several propagating modes are possible. With the work, we aim to further demonstrate the control of light with liquid crystal disclination lines.

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## Liquid crystal gyroids as photonic crystals

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The gyroid triply periodic minimal surface separates space into two congruent and oppositely chiral labyrinths of passages. This makes it an interesting template for optically active photonic crystals. The liquid crystal gyroids are designed as composite optical materials, where one labyrinth of passages is taken to be solid dielectric, whereas the other complementing labyrinth of passages is taken to be filled by chiral or achiral nematic liquid crystal, with the intermediate gyroid surface imposing homeotropic surface anchoring.

In this work chiral and achiral nematic gyroids are explored as photonic crystals using mesoscopic free energy minimisation to determine the nematic orientational profiles and eigen-problem Bloch-type solving of wave equation to calculate the photonics bands. The nematic inside the gyroid is shown to exhibit a variety of possible ordered, semi-ordered or completely disordered complex networks of topological defects. This broad diversity of nematic states leads to a rich structure of photonic bands, which can be tuned by the liquid crystal volume fraction and the cholesteric pitch. The variation of this two parameters provides the control over direct and indirect band gaps [1].

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## Compensated cholesterics of helical mesogens: insights from simple microscopic models

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We study the pitch of cholesteric assemblies of helicoidal patchy cylinders as a generic model for chiral biopolymers and helix-shaped colloids. Using microscopic theory [1] and computer simulation [2] we find that the handedness of the chiral assembly may spontaneously flip sign upon changing the system density or temperature while preserving the chiral features of the individual particles. We show that these inversions are generic and can be expected in cholesteric phases of both thermotropic and lyotropic origin. The mechanism underpinning the symmetry inversions can be explained in terms of an antagonistic effective torque acting between helical rods. We discuss the role of director fluctuations and the impact of concentration fluctuations on the topology of the helicoidal director field [3].

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## Impact of CdSe-ZnS quantum dots upon the nematic liquid crystalline orientational order

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Nematic Liquid Crystals (LCs), made of anisotropically shaped molecules, are mesophases characterized by long range orientational order, intimately related to their macroscopic anisotropic properties. Nanoparticle doped LCs have been widely investigated during the last two decades focusing mainly on the impact of nanoparticles on orientational, translational and phase ordering properties.

We report on the impact of spherical nanoparticles upon the nematic order as a function of concentration. The thermotropic LC 4 - n - pentyloxyphenyl - 4' - n - octyloxybenzoate (5OP8OB) exhibiting a wide-range nematic phase of 20 K has been studied. Nanocomposite 5OP8OB systems with three different concentrations of semiconducting spherical CdSe-ZnS quantum dots have been prepared. We have measured the degree of orientational ordering in the nematic phase [1] in composites and in the reference pure sample. The order parameters  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  have been determined as a function of the temperature by polarized micro-Raman spectroscopy [2]. Additionally, the parameter  $\langle P_2 \rangle$  has been also calculated from birefringence measurements performed by Polarizing Optical Microscopy. The results from both methods are in satisfactory agreement. It has been found that for a large enough concentration of the quantum dots the orientational ordering is relatively strongly suppressed. On the other hand temperature behaviors exhibit qualitatively bulk like behavior and relatively weak shifts in isotropic-nematic phase transition temperature. We have developed a simple model yielding qualitative explanation of observed phenomena.

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## Light modulation by electric field reorientation of liquid crystal graphene

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Graphene oxide (GO) has emerged as a very performing new member of the liquid crystal (LC) family with an extremely low concentration threshold for LC phase formation but also for its responsiveness to electric fields due to a very high Kerr coefficient [1]. GO can be found as intermediate product during the preparation of graphene, finally obtained upon chemical reduction. This oxidative form of graphene has the great advantages of being dispersable in water due to the presence of hydrophilic functional groups, aspect that makes GO easy to handle but enables also the formation of stable dispersions that can exhibit LC phases.

Graphene, or reduced graphene oxide (r-GO) flakes are the final goal of the graphite exfoliation due to their attractive electrical conductivity. This property turns out to be attractive also for tunable LC graphene suspensions thanks to the expected higher dielectric anisotropy, thus greater response to electric fields, compared to GO flakes which are almost insulator. However, stable dispersions of r-GO are difficult to realize due to the tendency of aggregation of the hydrophobic graphene flakes in water after that the functional groups are removed. We have shown that, using surfactants during reduction, it is possible to achieve stable suspensions of r-GO that also form liquid crystal phases with macroscopic alignment induced by shearing and electric field application [2]. Modulation of light transmission could be also observed by application of very small fields onto r-GO LC suspensions obtaining higher induced birefringence than for GO suspensions, at the same field strength and for all investigated concentrations. Our results show that r-GO LC has indeed superior electro-optical performance but also longer-term stability compared to GO LC.

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## **Topic 4**

# **Polymers, Polyelectrolytes, Biopolymers**

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We present a novel multi-scale coarse graining approach,[1] suitable for mixtures of long chains and star polymers. The approach is based on a multi-blob description of the long chain, where each blob, representing  $N_0$  monomers, interact with the star polymer through an effective potential. Such effective interaction has been first calculated numerically for star polymers of different functionality  $50 < f < 150$  and different arm length  $50 < N < 150$ . Through a theoretical analysis of the numerical results, we provide an approximate, analytical form for the interaction potential, valid for stars of arbitrary functionality and arbitrary size. We test our approach, comparing the effective interaction between a star polymer and a long chain of length  $N_c$ , as well as the conformational properties of the chain, at both coarse-graining and monomer-resolved level. We find that the coarse-graining approach yields an excellent agreement with respect to monomer-resolved results.

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## Condensation and demixing in solutions of DNA nanostars and their mixtures

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The pivotal role played by DNA in biology cannot be understated. Its outstanding pairing specificity, embodied by the famous Watson-Crick mechanism, is at the core of its biological functionality. Exploiting such a specificity in synthetic applications, an idea which dates back to the seminal work of Ned Seeman in the 1980's, provides researchers from many different fields, ranging from nanotechnology to material science, with a new, powerful tool [1].

DNA can be used in colloidal systems as a coating agent, but also on its own to self-assemble all-DNA materials with controllable properties. In particular, short DNA strands with carefully designed sequences can self-assemble into well-defined constructs at intermediate temperature. These DNA constructs (nanostars) can, in turn, bind to each other in a controlled fashion to form higher-order structures. Recent experiments have demonstrated that DNA nanostars can be employed as experimental realisations of patchy particles [2, 3], which have shown promising properties as theoretical and numerical model systems for the synthesis of new soft materials such as empty liquids, reentrant gels and open crystals.

Here we present a novel mixed numerical/theoretical approach to efficiently evaluate the phase diagram of these objects. Combining input information based on a realistic coarse-grained DNA potential with the Wertheim association theory we derive a parameter-free thermodynamic description of these systems. We apply this method to investigate the phase behaviour of single-component and mixtures of DNA nanostars with different number of sticky arms, elucidating the role of the system functionality and of salt concentration. The predicted critical parameters compare very well with existing experimental results for the available compositions [4]. Our approach takes into account DNA-DNA interactions in a realistic fashion and therefore is very general and can be easily extended, *e.g.* to investigate the behaviour of all-DNA systems that incorporates DNA nanotechnology motifs such as hairpins and strand displacements.

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## Structure of ionic microgels driven by an alternating electric field: theory, experiments and simulations

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When a system of charged nanoparticles suspended in an aqueous solvent is subjected to an alternating electric field, the resulting ionic diffusion gives rise to complex, frequency dependent dielectric responses. Quite recently, the physical mechanisms behind the different relaxation modes of such dielectric spectrum of suspended microgels have been investigated both theoretically and in experiments [1]. From a coarse-graining perspective, we can think of the microgels as acquiring a frequency-dependent effective dipolar moment which results from the combined ionic and polymer responses to the applied field. Such induced dipole interactions are responsible for a number of complex particle conformations – ranging from string formation along the field to ordered solid-like structures in the perpendicular plane – which can be tuned by changing both field strength and frequency [2, 3, 4]. In the present work, a theory is proposed to predict such structural features based on the induced dipole interactions. The proposed effective description allows one to partially account for the different dielectric regimes based on the assumption that only a reduced fraction of counterions are polarized by the field at different oscillation modes, thereby screening the microgel effective dipole interactions. Using the Ornstein-Zernike formalism and molecular dynamic simulations, it is shown that the effective description is able to accurately describe most of the structural transitions observed in the experiments.

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We explore the structural properties of magnetically functionalized star-polymers by means of computer simulations. The functional units are formed by superparamagnetic nanoparticles and are located only at the end of polymeric arms that are joined at the central core of the star-polymer. The natural steric interactions between the polymeric chains, which under good solvent conditions and low star density result in the characteristic star-shaped conformation, have to compete with the magnetic interactions stemming from the functionalized end-groups. The strength of this directionally dependent interaction is controlled by means of an external magnetic field, that for the case of superparamagnetic nanoparticles leads to perfectly parallel oriented magnetic dipoles. On augmenting the strength of the external field their interaction causes an internal self-organization that results in the formation of one or more magnetic chains that can be viewed of as reversibly bonded clusters or patches. The thus formed patchy-like particles are characterized by the number of the magnetic dipole chains and their average length, which can be controlled by the strength of the external magnetic field, the functionality of the star-polymers, and the length of the polymer chains.

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Dendrimers are synthetic macromolecules possessing a highly branched and regular internal structure. They are synthesized in a step-wise fashion by repeating units from various central multifunctional cores, on which radially branched shells called generations are covalently attached. Charging these dendrimers leads to conformational responsiveness, one of the most important ingredients for envisioned applications of the same, which is essentially lacking for their neutral counterparts.

Recently, Dan Luo and co-workers at Cornell University synthesized dendrimer-like DNA (DL-DNA) from the enzymatic ligation of Y-shaped DNA (Y-DNA) building blocks [1]. These charged DNA dendrimers are novel macromolecule aggregates, which hold high promise in bringing about targeted self-assembly of soft-matter systems in the bulk and at interfaces.

Inspired by these findings, we study systems of such DL-DNA molecules in order to advance the theoretical analysis of novel self-assembled structures. First, we simulate a single DL-DNA molecule, whose base-pairs are modeled by charged monomers. Their interactions are chosen to mimic the equilibrium properties of DNA correctly. We then employ MD simulations to measure the dependence of equilibrium properties, e.g. the influence of salinity, the tensor of gyration, and form factors, on the dendrimer's generation. The obtained results are compared to experiments.

In the future, we plan to use DL-DNA to investigate the phenomenon of cluster crystals in the bulk [2], a novel form of solids with multiple site occupancy. Furthermore, we want to study two-dimensional surface ordering of low-generation DL-DNA and Y-DNA with tunable rigidity around the junction point [3].

The study of these charged dendrimer-systems is an important field of research in the area of soft matter due to their potential role to various interdisciplinary applications [4, 5], ranging from molecular cages and carriers for drug and gene delivery in a living organism to the development of dendrimer/dendron-based ultra-thin films (monolayers and multilayers) in the area of nanotechnology.

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# Magnetically Functionalized Star Polymers in Equilibrium and under Shear

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Star polymers are macromolecules consisting of a central site, attached to which are a number  $f$  of linear polymer chains, called “arms”. Depending on the chemical composition of the arms, the polymer stars exhibit intriguing features, both in isolation and in concentrated solution. If, for example, one makes the fraction  $\alpha$  of the polymers closest to the central site of each arm solvophilic, and the remainder of the arm solvophobic, one finds in computer simulations that the solvophobic parts aggregate into patches, the number of which per polymer star is determined by  $f$  and  $\alpha$ . These so called telechelic star polymers can connect to one another via their patches, resulting in aggregate crystals. The stability of the crystal lattice (e.g. diamond or simple cubic) is dependent on the coordination number, i.e. the number of patches per star, and as such ultimately by  $f$ ,  $\alpha$ , and the solvent quality. [1]

While one may be able to manipulate the latter parameter in an experiment, the functionality  $f$  and the solvophilic arm fraction  $\alpha$  are set during synthesis of the star polymers, and as such cannot be changed in-situ. To provide an additional, versatile avenue by which one can control the inter-star interactions, we study in this work an alternative type of star polymers: Instead of triggering aggregation of parts of the stars via solvophobicity, we perform computer simulations of stars where each arm is homogeneous, except for the free ends of the arms, which carry super-paramagnetic dipole moments. This way, one can employ fine-grained control of the attraction of the arms’ ends by applying an external magnetic field, the magnitude of which controls the interaction strength of the dipoles. The direction of the external field plays an important role in the case where we impose external shear flows of varying shear rates on the system.

We use Multiparticle Collision Dynamics (MPC) simulations [2, 3] to efficiently model the explicit solute and allow for hydrodynamic interactions, and couple MPC to a Molecular Dynamics (MD) treatment of a coarse-grained model of the star polymers, the constituents of the polymer chains being represented as a number  $N$  of effective monomers. This approach allows us to scan parameter space and examine static and dynamic properties of dilute solutions, such as the number of patches, their alignment with the shear flow direction, measures of the shape of the overall star, and relaxation times. We present and interpret the data gathered, and discuss implications for possible applications, such as tunable mixers in microfluidic devices.

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## Telechelic star polymer micelles under shear

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Star polymers are interesting both for their industrial applications as well as from a scientific perspective as they constitute a bridge between colloids and polymeric chains[1]. Structurally star polymers are composed of a number of polymeric chains (called arms) which all have one end attached to a single central point. If in addition the outer ends of each arm are functionalized so that they can attach to each other, the star is called telechelic (TSP). Single telechelic stars can, under particular conditions, self-assemble into aggregates where the functionalized parts of multiple arms come together to form attractive patches. A particular type of these aggregates that appears for low number of arms is the one exhibiting only one attractive patch, the so-called “watermelon” structure [2]. Watermelon structures can further assemble to form micelles. The micelles contain, at the core, the attractive patches bound together which are shielded by the non-interacting parts of the stars. Using Molecular Dynamics we investigate the thermal stability of these aggregates and their behaviour under shear.

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## Closing a Gap - Polymer Ring Brushes pushed together: a DPD simulation study

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Grafting polymers to a surface is of interest to many physicochemical areas and applications, such as colloid stabilisation, wetting, adhesion, chromatography, biocompatibility and others. Recent experimental methods allow the production of well-defined surface-grafted polymer nanoparticle systems without free chain-ends [1], i.e., grafted polymer loops or rings. In the present investigation, equivalent situations are studied making use of computer simulations based on Dissipative Particle Dynamics [2,3] (DPD).

DPD is a highly efficient, coarse grained, method smoothly covering length scales from several nanometers up to the mesoscale region. In order to reproduce the behaviour of adsorbed polymers an attractive interaction between one (or in case of loops both) chain end(s) and the surface, represented by a soft wall, is introduced as well. Aim of the study is the comparison of properties of loops and rings to those of linear chains as functions of surface coverage free chain concentration and inter particle distance i.e : from isolated particles to polymers in slit like confinement.

The results show that with increasing grafting density, loops and rings become more and more rodlike in structure and increase the layer thickness in the same way as linear chains do. A rise in concentration of free polymer chains results into a compression of the brush. Decreasing the inter particle distance leads to an increase in pressure exerted by the grafted polymer on the wall. A comparison of the structural effects and possible interpenetration for linear chains and rings will be shown in detail.

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## Study of silica nanoparticles / polymer hydrogel nanocomposite

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The design of nanocomposite materials is a fast-growing field with many novel and exciting materials with a wide array of mechanical, thermal, and catalytic properties, such as composite formed by polymer hydrogels and silica nanoparticles. In particular, the coupling between chemistry of adsorption and mechanical properties has been poorly explored. Recently a way was found to glue together two polymer gels using a dispersion of silica nanoparticles (NPs). Indeed, it is difficult to glue together polymer gels because it requires chemical reactions, pH changes or heating. Hence it is proposed for the first time that spreading a droplet of a silica NP solution on the surface of one gel and then bringing a second gel into contact with it leads to strong adhesion between the two gels of poly(dimethylacrylamide) (PDAM). Intriguingly, polyacrylamide (PAM) does not adsorb onto silica whereas PDAM adsorbs.

Through coarse grained molecular dynamics, based on inputs from quantum calculations and all-atom simulations, we characterize qualitatively and quantitatively the structure, dynamics and mechanical properties of such nanocomposite material. We focus particularly on an investigation of the different behaviour of PAM and of PDAM with regards to their adsorption on the silica surface. We look into the dynamics and the interaction energy of the polymer chains surrounded by water close to the nanoparticle's surface, compared to those of the bulk of the hydrogel.

# Conformation evolution of hydrophobic polyelectrolyte in aqueous solution as a function of solvent quality: a SANS study

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In this work, we studied the conformation evolution of an hydrophobic polyelectrolyte in aqueous solution and in a semi-diluted regime as a function of the improvement of solvent quality, by adding small amounts of good solvent for the backbone "THF" and by THF treatment (replacing the added amount of THF by the same amount of water). The polyelectrolyte studied is poly (sodium styrene-co-styrene sulfonate) at different charge rates above the Manning condensation threshold and whose hydrophobicity is correlated with the chemical charge rate  $f$ .

The form factor of poly (sodium styrene-co-styrene sulfonate) is measured by Small Angle Neutron Scattering using the Zero Average Contrast method. The main result is the form factor of the hydrophobic polyelectrolyte shows contributions of spherical entities as well as extended chain parts, as was the case of previous studies dealing with investigation of chemical charge rate  $f$  in pure water [1]. Moreover, the hydrophobic polyelectrolyte chain evolves from a collapsed conformation that can be simulated with a Pearl-Necklace-Like conformation [2] towards a stretched chain conformation that can be simulated like a vermiform chain, as the solvent quality is improved by adding small amounts of THF to the aqueous medium. As a consequence, the radius of gyration  $R_G$  of the polyelectrolyte chain increases, the apparent degree of polymerization  $N_w$  decreases and the pearl diameter of the Necklace  $D_{\text{pearl}}$  decreases.

Moreover, THF treatment showed no effect on the diameter of the pearls  $D_{\text{pearl}}$ , the radius of gyration  $R_G$  of the chain and the apparent degree of polymerization  $N_w$  were slightly affected by THF treatment, which shows that the pearl necklace conformation is at equilibrium state in water.

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## Polymer brush/gold nanoparticle composite materials for the application as colorimetric sensors

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Polymer brushes are polymers tethered to a surface or interface by one end, which at sufficiently high grafting densities show a stretched conformation away from the surface. This stretching is often responsive to environmental conditions and that makes them a suitable candidate for the design of smart coatings. Beside their responsive behavior, they also can be used as matrices for the immobilization of nanoparticles. Incorporating gold nanoparticles (AuNPs) in polymer brushes results in nanocomposite materials with interesting nanosensor properties due to the fact that AuNPs exhibit surface plasmon resonance (spr). In addition, the interparticle distance can be used to shift the spr in a certain way. Therefore, AuNPs can act in two ways: They can be considered as colorimetric sensors to detect changes in the polymer brush matrix or stimuli-sensitive AuNPs trigger the structure of the polymer brush matrix. Therefore, the distribution of AuNPs within the polymer brush is of great importance with respect to the optical properties [1].

In this work, the assembly of charge switchable AuNPs inside neutral charged Poly(N-isopropylacrylamide) (PNIPAM) brushes will be discussed. The 5 nm AuNPs are capped with mercaptopropionic acid (MPA,  $pK_a$  5.5) which bears a carboxylate group and is either protonated (uncharged) or deprotonated (negatively charged) depending on the pH. Some recent efforts have been made to control particle uptake and distribution in weakly charged (PDMAEMA)[2][3] and strongly charged (PMETAC)[4] polymer brushes due to electrostatic interaction between particle and brush. In contrast, PNIPAM brushes are neutral charged and can only interact via H-bonding with the AuNPs. Here the focus is on understanding how protonating and deprotonating of the AuNPs affect particle embedding and stability in PNIPAM brushes.

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## Bimolecular reactions in stimuli-responsive nanoreactors

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Responsive nanoreactors are composed of nanoparticles coated by a stimuli-responsive polymer shell, whose permeability affects the catalytic rate of the reaction occurring at the nanoparticle's surface. In this work [1], we provide a general theory for surface-catalyzed reactions for a wide class of emerging nanoreactors, explicitly including shell permeability effects for bimolecular reactions within the framework of the Debye-Smoluchowski rate theory [2,3]. The permeability of responsive polymer gels can be studied experimentally and in terms of computer modeling and theory [1,3-6]. We study two main scenarios representing typical catalytic reactions. The first, where two species diffusing from a bulk solution react at the catalyst's surface; the second where only one of the reactants diffuses from the bulk while the other one is produced at the nanoparticle surface (e.g., by light conversion [5]). We find that in both scenarios the total reaction rate is formulated mathematically by exactly the same way, where the diffusional fluxes of the different reactants are strongly coupled. Thus, the conventional unimolecular theory, giving the total rate as the reciprocal sum of the diffusion and reaction times [3], is just valid when one reactant diffuses much faster than the other. We finally show how this theory can be applied to rationalize experimental data on the reduction of nitrobenzene by borohydride at gold nanoparticles in responsive hydrogel-based nanoreactors [6].

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# Association of alkali metal and tetraalkylammonium counterions to poly(thiophen-3-ylacetate) as seen by NOESY NMR spectroscopy and molecular dynamics

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Poly(thiophen-3-ylacetic acid) (PTAA) is a typical representative of conjugated polyelectrolytes, i.e. of polyelectrolytes with conjugated main chains. Due to their favourable physical properties, these polymers are recently the subject of intensive basic and applicative studies. During recent studies [1] of thermodynamical (osmotic coefficients) and transport (electrical conductivity, transport numbers) properties of aqueous solutions of alkali metal salts of PTAA it was found that the fraction of alkali metal counterions bound to PTAA is almost insensitive to the kind of the counterion. While in the consequent study [2] this finding was further confirmed by measurements of self-diffusion coefficients for alkali metal counterions, a notable difference in extent of binding of different tetraalkylammonium (TAA) counterions to PTAA was found, being probably propelled by hydrophobic interactions.

This research focus on the binding mode of different types of counterions (alkali metal and TAA) to PTAA. In this regard, molecular dynamics (MD) simulations and NOESY NMR spectroscopy were used. MD calculations were carried out for two PTAA oligoions of different length and for two concentrations of monomeric units using Desmond program. PTAA molecule was described by OPLS-T-SB force field [3], while water molecules were treated within SPC model. From results of MD simulations, NOESY-spectra were calculated [4]. NOESY spectra were measured for <sup>1</sup>H using Bruker Avance DRX 500 NMR spectrometer operating at 499.76 MHz. Concentrations of studied solutions were 0.2 mol/dm<sup>3</sup> and the optimal mixing time was determined to be 0.5 s.

The comparison of experimental and MD results shows that although some features obtained by MD simulations are rather closely correlated with theoretical predictions (bound alkali metal located in the vicinity of carboxyl group, TAA counterions at hydrophobic backbone of PTAA), MD simulations failed in the prediction of extent of binding of different kinds of alkali metal counterions to PTAA polyion. This is hardly a surprise taking that also most advanced MD simulations are not capable of predicting Hofmeister series [4]. We assume that also use of more sophisticated water model would not describe extent of alkali metal counterions properly [5,6].

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## Weak Intramolecular Complexation within Star-like Copolymers: A Generic Model

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Weak attractive interactions can lead to intramolecular complexation. Experimentally, it was found that such an intramolecular complexation occurs in systems of poly(propylene oxide) (PPO) and poly(dimethylaminoethyl methacrylate) (PDMAEMA) [1]. It was found that differences in local mutual segment density in linear block-copolymers and miktoarm star polymers of the two components effect the complexation. A complexation of the PPO chain in the miktoarm stars was found for conditions under which the linear polymer is not complexed.

To rationalize these observations a generic bead spring model is employed. The polymers are modeled using a bead spring model with two types of hard sphere beads. The different spheres interact through an attractive Lennard-Jones Potential, mimicking the weak attractive interactions. This model allows for easy variation of architectural parameters (topology and composition) as well as the effect of these parameters on the complexation and the corresponding polymer structures. Using Monte Carlo simulations, the structures of miktoarm star-shaped polymers and diblock copolymers were investigated as a function of the attractive strength.[2] At intermediate interaction strengths, the complexation is more pronounced in miktoarm star polymers than in diblock copolymers.

By additionally comparing different compositions, it is shown that the influence of the composition increases with the interaction strength. The same degree of complexation of a diblock copolymer can be achieved by a miktoarm star of lower molecular weight in accordance with experimental observations.[3]

To deepen the insight into the mechanism, the miktoarm star topology is gradually changed into a graft copolymer topology giving insight into the role of the topology on the complex formation. In addition the possibility to affect the complexation by adding non-interacting polymeric spacers are presented.

Also the intramolecular aggregation behaviour is investigated by simulating multiple complex forming miktoarm star polymers. It is shown that complexation can lead to an micellization behaviour which differs from the micellization behaviour known from segregating amphiphilic polymers.

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## Colloidal stability and reversible aggregation of oxidized tannins

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Physical-chemical interactions involving tannins continue to intrigue not only food scientists and pharmacologists, but also biophysicists and chemists. To cite in first place is a spectacular efficiency of some plant tannins against amyloidogenesis of several pathogenic proteins, closely related to the ability of tannins to modify protein physical structure. These phenomena are also the basis of astringency of some plant-derived beverages: wine, beer, apple cider, tea etc. Moreover, propensity of tannins to self-aggregate and/or to denature proteins determines the colloidal stability of tannin-rich suspensions, which is relevant for their bioavailability and ageing ability, issues of interest in pharmaceutics and food technology.

We focus here on chemical structure and physical properties of tannins prone to self-associate under oxidative and/or cooling stress. For this purpose we use tannins from procyanidins family: poly-epicatechins, extracted from apples. These compounds can represent more complex tannins from many fruits, but remaining still sufficiently simple homopolymers to allow for serious quantitative physical analysis.

First result is that some oxidized tannin species are insoluble at concentrations of the order of g/L, while native tannins are systematically highly soluble. Namely, our SAXS data reveal the size and the structure of both, native (T2) and oxidized fraction (T1) for oligomeric (DP of 1 to 7) and polymeric (DP up to 225) tannins. T2 fraction contains individually solvated molecules, while T1 contains both, soluble and aggregated tannins. Polymer conformations and the composition of the solvation layer in mixed water-ethanol solvents are coherent with general statement that tannins upon oxidation increase their aggregation propensity via hydrophobic means.

Second result is based on a simple observation that hazes in some apple alcoholic beverages are reversible upon heating cycles, revealing a non-covalent nature of interactions. In order to investigate the effect, model solution of tannins with controlled DP and oxidation degree were submitted to a series of temperature ramp-descend cycles (typically 4°C-60°C-4°C) and studied by DLS. From LS data in descending/ascending T-jump, kinetics of aggregation/fragmentation was extracted and analysed as function of the initial/final temperature. Both the aggregated mass fraction and the self-association rate are temperature-dependent, which opens perspectives for systematic studies of based on fractional precipitation of tannins exposed to controlled oxidation.

## Evolution and Correlation of Morphology and Mechanical Properties in Polymorphic Phases of PVDF

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Poly(vinylidene fluoride) (PVDF) is attracted research interests not only because of its high piezo, pyro and ferro electric properties but also due to its existence in several polymorphic phases such as  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  [1]. Synthesis of electroactive  $\beta$  phase is the highest interest in research community in applications point of view. Formation of these polymorphic phases depends on the molecular interactions between polymer chains under different synthesis conditions. In order to achieve desired properties, it is important to understand the correlation between the crystal structure and arrangement of polymer chains while crystalizing this polymer from its melt and solution [2].

In this work we successfully prepared and characterized polymorphic phases of PVDF and tried to understand its morphology, mechanical behaviour evolution with the observed dielectric nature. Interestingly it is found that among the polymorphic phases electroactive  $\beta$ - phase is found to be mechanically softer. Young's modulus and hardness are found to be around 4 GPa and 170 MPa respectively. It is found that among these phases, electroactive  $\beta$ -phase is showing higher dielectric constant value at room temperature. Correlation between morphology, mechanical and dielectric properties will be discussed in detail.

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## Comparison between micro- and macro-scale kinetics of water sorption in textile fibers

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Physical properties of textile fibers are customarily probed by standardized instrumental methods based on macroscopic approaches [1]. Consequently, they require rather bulky equipment and are usually also quite time consuming. On the other hand, fast and simple micro-assay-based analytical techniques are rapidly gaining in importance in chemistry, biology, medicine and many other fields, therefore it is expected that they will soon experience increasing uses also in textile engineering.

One of crucial properties of textile materials is their capacity to absorb water-based liquids and the rate of the associated liquid sorption and desorption processes. In our recent investigation we have shown that characteristic times associated with microscale sorption properties can be readily resolved by optical video-microscopy-based analysis performed on single fibres [2-4]. In this contribution we present a comparison between the standard macroscopic method for determination of sorption kinetics and its video-microscopy-based counterpart. Experiments were performed with polyester fibers designed for thermoregulative-type fabrics. We show that both methods give similar values of the average sorption rate of water in the selected material and discuss their advantages and disadvantages from the point of view of sample preparation and instrumental requirements.

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## Elastomeric PDMS stiffness influence on adhesion, culture and mechanics of endothelial cells

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Atomic force microscopy (AFM) in Force Spectroscopy mode was applied to characterize the mechanical properties of elastomeric silicone polydimethylsiloxane (PDMS) films, commonly used as a substrate in cell culture, prepared under different conditions. The analysis was done over different specimens of PDMS whose final composition was tuned by adjusting the pre-polymer/cross-linker ratio (5:1, 10:1, 20:1, 30:1 and 50:1) in the initial mixture, which regulates the final material properties (e.g. stiffness, elasticity). In order to quantify the mechanical behavior of the PDMS, the Young's modulus as well as the sample's spring constant (related to stiffness) were calculated from the obtained force-distance curves. In addition, the naturally hydrophobic siloxane films aforementioned could also be converted into hydrophilic interfaces by exposure to oxygen plasma, a treatment playing a key role on the stiffness, adhesion and final functionality of the film, as observed for incubation of HUVEC endothelial cells on top.

Results show the cross-linker concentration-induced impact on substrate mechanics for all the ratios analyzed. Also plasma activation of the film affects the film performance by an overall hardening and equalization of the calculated elastic moduli..

## Coarse-grained Mie force field for the molecular dynamics simulation of water - polyethylene glycol systems

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The study of liquid-liquid immiscibility is of fundamental importance in understanding biological systems. Coarse-graining approaches enable the simulation of larger length and time scales necessary to study complex biological phenomena using molecular-dynamics simulation. In this work, the behaviour of the pharmaceutically relevant [1], and prototypical biopolymer, polyethylene glycol (PEG) in water is considered. This system has been previously studied and coarse-grained using iterative boltzmann inversion by Prasitnok and Wilson [2]. In our model, however, a top-down coarse-graining approach is used and the focus is on capturing the system's closed-loop liquid-liquid equilibrium behaviour [3] over a larger temperature range.

The group contribution statistically associating fluid theory (SAFT- $\gamma$  Mie) [4] equation of state (EoS) has been used by Lobanova et al. [5] as a top-down coarse-graining approach to develop non-associating models for the simulation of mixtures of carbon dioxide, water and n-alkanes. In this work, the application of this methodology is extended to polymer-water systems with the aim to study liquid-liquid immiscibility of aqueous solutions of PEG.

Using the SAFT- $\gamma$  Mie EoS the intermolecular force field parameters are estimated from target pure component vapour pressure and liquid density data as well as liquid-liquid equilibrium data of water-PEG mixtures. A temperature dependent CG attractive interaction between the polymer and water segments is found necessary to capture the change in the degree of hydrogen bonding of the system with temperature, the process responsible for the lower critical solutions temperature (LCST) of the water-PEG mixture [6]. Work by Rahman et al. [7] on alkanes suggests that including intramolecular bonded interactions, not accessible from the SAFT formalism, improves the accuracy of the model in predicting structural and transport properties. The effect of the inclusion of bonded force fields developed from atomistic simulations is investigated and compared to fully flexible model of the SAFT theory. The developed force fields are used to study the behaviour of the system in molecular dynamic simulation allowing for the calculation of structural properties like the radius of gyration, which are not directly obtainable from the SAFT theory.

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## Temperature phase behaviour of $\text{PMEO}_2\text{MA}$ -*b*- $\text{POEGMA}_{300}$ co-polymer in water by molecular dynamics

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The aim of this study is to investigate the thermoresponsive phase behaviour of poly(2-(2-methoxyethoxy)ethyl methacrylate)-*b*-poly(ethylene glycol) methyl ether methacrylate ( $\text{PMEO}_2\text{MA}$ -*b*- $\text{POEGMA}_{300}$ ) co-polymer with 20/5 block length ratio by atomistic classical molecular dynamics. The co-polymer is investigated at temperatures selected below and above the so-called 'lower critical solution temperature' (LCST) value. POEGMAs, which are a type of thermoresponsive polymers, exhibit LCST behaviour in water. While they are water-soluble at low temperatures, they become insoluble when the temperature exceeds above the LCST value. Conformational changes play a critical role on the determination of temperature-dependent functions of these polymers. POEGMAs have a strong potential in use for controlled drug release and in vivo delivery of genetic materials. Therefore, it is quite important to know how these polymers behave in water, in order to analyse their behaviours in physiological environment. However, the molecular details of the LCST phase transitions of POEGMA systems and polymer-water interactions have not yet been fully understood. In this study, the structural and dynamic properties of the phase behaviour of this co-polymer through temperature is analysed by looking radius of gyration, RMSD, number of first shell water molecules, RDF and hydrogen bonds.

## Statistical theory of co-nonsolvency: comparison with md simulation results

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Co-nonsolvency is one of the most enigmatic phenomena in polymer physical chemistry. Co-nonsolvency is an insolubility of a polymer in a binary mixture of good solvents [1]. In the dilute polymer solutions co-nonsolvency manifests itself as the coil-globule transition at the certain value of the mixed solvent composition [1]. Importance of the co-nonsolvency is related to the fact that it is generic physical phenomenon, taking place in both the solutions of biological macromolecules [2] and the solutions of synthetic polymers [3]. Despite the great efforts of both the theoreticians [1-3] and experimentalists [4-6] in the co-nonsolvency investigation, its microscopic mechanism and thermodynamic nature remain partially misunderstood. In present report recently developed statistical model [7] of the flexible polymer chain immersed to the binary mixture of good solvents, predicting the co-nonsolvency, i.e. polymer chain collapse at the certain value of the co-solvent mole fraction will be presented. The co-nonsolvency thermodynamic nature will be also discussed. A direct comparison between the theoretical results and the available in the literature MD simulation results [5-6] will be demonstrated.

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## Light induced patterning in transparent polydiene solutions

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Light-matter interactions have been at the focus of scientific activity for centuries. Recently, complex fluids have attracted increased attention owing to their intricate response to optical fields. An intriguing case of a nonlinear optical response was revealed in polydiene solutions [1]. The unexpected formation of permanent structures upon mild laser illumination in transparent, viscous and non-absorbing cis-1,4 polydiene solutions in organic solvents of lower refractive index (e.g. hexane, toluene) has been observed. The structure formation arises from local variations in the refractive index due to local changes of polymer concentration.

It was observed that local refractive index can either increase or decrease upon irradiation, depending on the solvent environment [2, 3]. Here, we present the phenomenology of polydiene/tetrahydrofuran (THF) semidilute solutions. The response of the polydiene solutions to red laser light were observed through phase contrast microscopy. In THF solutions, the irradiation leads to a local decrease of refractive index ( $\delta n < 0$ ) and the formation of a conical pattern with lower refractive index than the surrounding solutions. This pattern is very different and larger than the fibrillary polymer enriched patterns, observed in most good solvents. This difference is a consequence of the self-defocusing of the irradiation beam in THF, to be opposed to the self-focusing, present in most other solvents. The formed pattern can be extracted through rinsing procedure. Spectroscopic techniques were utilized to characterize the light induced structures, in order to investigate potential chemical changes due to laser irradiation.

The case of polydiene solutions in mixture of THF and hexane, in different ratios will be shown. The co-existence of self-focusing and self-defocusing cases was observed at the beginning of the irradiation, but at longer times of irradiation self-focusing appears to dominate when hexane ratio is large enough. Polydiene/ THF solutions provide a unique example of patterning in soft matter, so the elucidation of the nature of coupling behind this peculiar effect could open the prospect of polymer solutions as materials for lithography.

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# Polyelectrolyte Behavior of G-Quadruplex DNA Structures

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Guanine-rich DNA sequences are able to self-assemble into highly complex four-stranded G-quadruplex structures that are based on the formation of (G:G:G:G)-tetrads. These structures are interesting because of their biological role, since they are found in human telomeres responsible for cell transcription and translation. Besides that, if G-quadruplexes are grown into long continuous G-wires on solid substrates, they provide a promising element for various applications in nanotechnology, particularly in molecular electronics.

In aqueous solutions G-quadruplexes behave as strongly charged polyions with 4 negative charges per 0.34 nm. Their solution dynamics, as studied by dynamic light scattering (DLS), exhibits two diffusive modes [1]. The faster DLS mode represents a cooperative translational motion of the polyions and its diffusion coefficient shows a typical polyelectrolyte behavior as predicted by the coupled mode theory, if counterion condensation is taken into account [2]. The addition of ions results in complex solution dynamics induced by competition between cation-promoted self-assembly and screening effects. The slower DLS mode arises from the diffusion of large globular clusters and is not directly related to G-quadruplex formation. Similar slow modes have been reported for a variety of polyelectrolyte solutions including DNA, but their origin is still not resolved [3].

We studied a set of G-rich oligonucleotides with a varying number of GC-termini in aqueous solutions (GCGGTG<sub>4</sub>TGGCG, GCGGTG<sub>4</sub>TGG, GGTG<sub>4</sub>TGGCG, and GGTG<sub>4</sub>TGG). Previous atomic force microscopy studies showed the ability of similar sequences to form long G-wires on mica substrates [4]. We proved that in aqueous solutions these sequences form G-quadruplex structures by UV-Vis spectroscopy, while their polyelectrolyte properties were investigated by changing the polyion concentration and by increasing the added NaCl concentration. When a large amount of salt was added, phase separation was observed.

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## Towards Predicting Protein Aggregation in Biopharmaceuticals

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Understanding protein aggregation is an open problem in the development of antibody therapeutics, as stimulated by the rapid development of biopharmaceuticals in recent years [1, 2]. Biopharmaceuticals are proteins for use in medical treatment of various conditions such as rheumatoid arthritis, Crohn's disease, breast cancer, psoriasis and others. Non-native irreversible aggregation of proteins is particularly relevant today in the biopharmaceutical industry as it affects both production and long-term storage. Different mechanisms of aggregation for numerous therapeutic proteins have been proposed. Aggregated protein particles decrease the effectiveness of the drug and are associated with other risks, such as increased immunogenicity.

The purpose of this work is the characterization of the monoclonal antibody (mAb) aggregation process and identification of stability parameters that could be used as indicators/predictors of aggregation propensity with an emphasis on a large number of samples and low protein material consumption.

Two different stability parameters were measured for two different IgG subclasses in various formulations. Colloidal stability was assessed with dynamic interaction parameter  $k_D$ , obtained via dynamic light scattering measurements [3]. Conformational stability of mAbs was estimated with denaturation temperature measurements, obtained with the means of differential scanning calorimetry. The prediction capability of these parameters was assessed with a separate study of aggregation, which was induced by exposing the mAbs at different concentrations to thermal stress. The extent of aggregation was measured with size exclusion chromatography.

The dynamic interaction parameter was found to be a promising predictor of aggregation propensity of monoclonal antibodies. High temperature stress of mAb samples revealed that monoclonal antibodies followed first order aggregation kinetics, which suggests that the rate-limiting step of monomer loss was unimolecular. The meaning of using an intermolecular interaction parameter for prediction of what is essentially a unimolecular process is also discussed.

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## Simulation and experimental analysis of the structure and antimicrobial activity of linear peptoids

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Peptoids are a class of peptide mimetic molecules where the side chain is appended to the backbone amide nitrogen atom rather than the alpha carbon. As a result peptoids are not able to form the hydrogen bond stabilized helices which are typical of peptides. However, incorporation of chiral and charged side chains results in helical structured peptoids that share some of the key characteristics of antimicrobial peptides (AMPs).

AMPs form part of the natural immune response system of many organisms and have been investigated as a new class of antimicrobial to combat the growing resistance to traditional antibiotics.[1] A combination of cationicity and amphipathicity enables AMPs to selectively disrupt and destroy pathogenic cell membranes. The peptoids discussed here are believed to be promising antimicrobial agents as their structural similarities to AMPs allow them to act via similar membrane disruptive mechanisms, but their structural differences afford them resistance to in vivo proteolysis to which AMPs are vulnerable. [2]

Here we investigate a library of linear, cationic peptoids each twelve residues in length containing chiral and charged side chains arranged with different periodicities. We aim to characterize the secondary structures formed by these peptoids and their interactions with lipid vesicles as models for biological membranes. Circular dichroism of these peptoids in water and octanol indicate that they adopt different helical secondary structural configurations in aqueous and organic environments. We also show that the peptoids interact with lipid vesicles of varying compositions. Molecular Dynamics simulations, performed using modified AMBER force fields are used to predict and analyze the structures formed by these peptoids. Simulations in water and octanol allow us to map the secondary structural preferences of the peptoids in these different environments.

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## Universal criterion for designability of heteropolymers

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Heteropolymers are important examples in material science of self-assembling systems [1, 2, 3, 4]. The technology for the synthesis and manipulation of such heteropolymers is already advanced, and it is nowadays possible to synthesize polymers made of up to 7 different monomers with complex pattern arrangements (e.g. block copolymers) [1, 2]. However, it is still not possible to design heteropolymers with control over the single chain self-assembling properties comparable to what natural bio-polymers, such as DNA and proteins, can achieve [5, 6]. Here we introduce a criterion to discriminate between polymers that can be designed to adopt a predetermined structure from polymers that cannot, and show that this criterion is fulfilled by the addition of few directional interactions to the monomers of the chain. The criterion is based on the appearance of a particular peak in the radial distribution function that dominates over the random packing of the heteropolymer. We show that the presence of such a peak indicates that it exists at least one pattern that will drive the system to collapse towards a specific target structure. Moreover, we show that the peak is a universal feature of all designable heteropolymers, as it is dominating also the radial distribution function of natural proteins. The criterion that we present can be applied to engineer new types of self-assembling modular polymers that will open new applications for polymer-based materials science.

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## Designing highly specific probes with tunable affinity

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Finding ligands able to bind with high specificity to a target protein is one of the major challenges in medical research, especially for the development of anti-cancer drugs [1]. Recently it was shown that therapies based on nanoparticles are ineffective [2] due to the difficulty of designing a particle coating which specifically recognizes cancerous cells. We aim at developing a novel computational protocol, based on the recently developed caterpillar [3] coarse grained model, to design proteins that can be used as effective coatings for novel cancer targeting nanoparticles. Key to the success of the targeting are proteins, which are highly selective towards the receptors on the cell membrane but with tunable binding affinity to reduce binding to healthy cells [4]. According to previous studies [5], performed with lattice protein models, such special protein sequences can be obtained by introducing destabilizing mutations in proteins designed to strongly bind to a target substrate. Since such control has not been attempted before on real proteins, we test the feasibility of our approach on a reference system first. We present results of our preliminary studies for a “protein like” pocket. First we design the sequences of both protein and pocket at the same time, in order to optimize the protein-ligand interactions. Then we monitor the binding affinity as a function of the percentage of destabilizing mutations in the amino-acids sequence of the protein.

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## Towards Stable Water-in-Water Emulsions through Interfacial Adsorption of Polyelectrolytes

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We propose a new strategy for the stabilization of water-in-water emulsions, namely the adsorption of polyelectrolytes at water–water interfaces. These interfaces are formed by spontaneous demixing of aqueous solutions of two incompatible polymers A and B into two phases, each enriched in one of the polymers [1–4]. Water–water interfaces have peculiar properties, as they may be charged [5], have an ultralow interfacial tension [6], and have a width of typically 10 nm [4]. Therefore it is complicated to stabilize water-in-water emulsions [7], composed of droplets rich in polymer A suspended in a continuous phase rich in polymer B, sharing water as a solvent.

Using numerical self-consistent field (SCF) calculations, we study the situation that polymer A is neutral and polymer B has a small electric charge, a common scenario in applications. Our calculations predict that an additional polyelectrolyte which is chemically similar to polymer A, but oppositely charged to polymer B, strongly accumulates at the water–water interface [8]. This interfacial complexation occurs already for low charge densities and surprisingly persists for high salt concentrations. We corroborate these SCF predictions with experimental observations. The adsorption of polyelectrolytes at the water–water interface may provide new routes to stable water-in-water emulsions.

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## On the mechanism of LCST and its variation with co-solvents in thermoresponsive polymer solutions

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Our interest lies in a class of thermoresponsive polymers which exhibit a Lower Critical Solution temperature (LCST) in aqueous solutions. The LCST transition is accompanied by a coil-to-globule transition at the single chain level. These polymer solutions also exhibit a decrease in the LCST with addition of co-solvents such as methanol, ethanol and propanol [1]. These interesting phenomena have been used in applications such as drug delivery, surface modification and self assembled structures. However, the underlying mechanism for the LCST and its variation with co-solvent is far from clear and a better understanding of the dominant interactions is required.

In this presentation, we will discuss our efforts to understand the dominant interactions governing the LCST and its decrease with co-solvents. We employ a combination of explicit solvent coarse-grained simulations, and mean field theoretical models based on the Kolomeisky-Widom potential [2]. Our results show that the competition between the entropy loss of the bound solvent, and the mean energy difference between the bound and bulk solvent is sufficient to explain the LCST [3]. We further observe that the variation of LCST with addition of co-solvent is driven by the decrease in the mean enthalpy of the bulk solvent. Another important point from our work is that the mean energetics of the solvent are more important in comparison to its structural details.

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## Modeling of pH-responsive polyelectrolyte solutions and gels

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We present the results of our simulation studies of the ionization behaviour and conformational changes in weak (pH-responsive) polyelectrolytes. In these studies we employed coarse-grained models in implicit solvent, and the reaction ensemble method to account for the ionization equilibrium. Using star-like polyelectrolyte under good solvent conditions we first investigate how the ionization varies with polymer architecture (number of branches and their length) [1]. We demonstrate that the non-ideal behaviour of weak polyelectrolytes gets enhance with dilution, quite opposite to the behaviour of low molar mass acids which become ideal when diluted [2]. Upon transition to poor solvent conditions we observe the formation of intra-molecular self-organized structures as a consequence of local coupling between the chain conformation and ionization equilibrium [3]. Finally, we develop a mean-field model for the swelling of weak polyelectrolytes in equilibrium with salt solutions, based on the analogy between gels and stars [4, 5], which we extensively validate against coarse-grained simulations. Using this model we show that pH inside the gel is lower by about one units than pH in the bulk solution as a consequence of the Donnan equilibrium. Within the mean-field model employed here, the leading contribution to the ionization response of the gel originates from the difference between the bulk and local pH, while the influence of gel architecture and connectivity appears less significant.

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Open molecular systems exchange mass, momentum, and energy with their surroundings. In this contribution, we will present our Open Boundary Molecular Dynamics (OBMD) method that opens up the boundaries of a molecular system and allows for equilibrium MD simulations in the grand-canonical ensemble as well as nonequilibrium fluid flow simulations[1]. The flow is introduced via an external boundary condition while the equations of motion for the bulk remain unaltered. To illustrate the robustness of OBMD, we will present simulation results of star-polymer melts in and out of equilibrium[2].

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## Process-directed self-assembly of copolymer materials

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The free-energy landscape of copolymer materials exhibits a multitude of metastable minima that correspond, e.g., to alternate periodic phases like hexagonally perforated lamellae, grain boundaries between domains of different orientations, or local defects. The barriers between these metastable states exceeds the thermal energy scale by far, resulting in protracted relaxation times. Thus, the thermodynamic stable morphology that corresponds to the absolute minimum often cannot be reached in experiments and simulations.

Process-directed self-assembly refers to strategies that reproducibly direct the kinetics of self-assembly from a starting, unstable state into a desired (meta)stable mesostructure by temporal control of thermodynamic variables, e.g., temperature, volume, or pressure. This strategy allows to access new morphologies, e.g., the bicontinuous I-WP network morphology [1] or the F-RD mesostructure [2] that do not correspond to stable bulk phases or control the orientation of the microphase-separated domains [3]. Using computer simulation of soft, coarse-grained models and dynamic self-consistent field theory calculations, we illustrate different processing protocols, e.g., pressure jumps [1], “al-chemical” conversion of segment species [2], solvent-annealing protocols [4], roll-casting [3], or spray coating [5], and demonstrate how the non-equilibrium, unstable initial condition dictates the spinodal kinetics of structure formation into a desired morphology. Since the initial kinetics occurs on the same time scale as the relaxation of the molecular conformations, chain conformations cannot be assumed to be in equilibrium with the instantaneous densities [1] – an assumption that is invoked in dynamic self-consistent field calculations – but additional order-parameters, e.g., the variance of the lowest Rouse-modes [3] or the fraction of bridges in multiblock copolymers [5], are required to characterize the rapid structure evolution out of a non-equilibrium state into the nearest metastable morphology.

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## Temperature responses of polymer mediated interactions

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In a recent publication, Feng et al. [1] reported interesting re-entrant solidification behaviour of colloidal particles in an aqueous solution containing polyethylene oxide (PEO). In this system, a crystalline colloidal phase, which is present at low temperatures, melts to a homogeneous fluid upon increasing the temperature. Further raising the temperature, however, eventually gives rise to a flocculated phase. We have developed a polymer density functional treatment of this system, based on a model for aqueous PEO solutions that was originally developed by Karlström [2] for bulk solutions. Here, monomers are assumed to be in either of two states,  $A$  or  $B$ , where  $B$  is more solvophobic than  $A$ . The degeneracy of the  $B$  state exceeds that of  $A$ , causing the population of solvophobic monomers to increase with temperature. This leads to a lower critical solution temperature, LCST. With solvophobic colloidal particles, this model displays the same qualitative temperature response as was observed by Feng et al. That is, at low temperatures,  $A$  type monomers predominate and one observes depletion interactions, whereas polymer bridging dominates at higher temperatures. Interestingly, the intermediate temperature regime is characterized by a polymer mediated interaction between particles which is *repulsive*. We show that interactions between colloids, mediated by neutral non-grafted polymers, generally follow the trend: attraction  $\Rightarrow$  repulsion (or vanishing interaction)  $\Rightarrow$  attraction as the surface affinity toward monomers proceeds from repulsive to attractive.

The same polymer model is also used to study structures and gelation in systems containing colloidal particles onto which PEO chains are grafted - a system that was studied experimentally by Shay and co-workers [3]. In agreement with their findings, we locate gelation at temperatures *considerably* below  $T_{\Theta}$ , and *far* below the LCST for such chain lengths. This gelation occurs also without any dispersion interactions between the particles. Interestingly, the polymer-induced interaction free energy displays a non-monotonic dependence on grafting density. We demonstrate that even minute amounts of adsorbed charge on the surface of the particles, can lead to dramatic changes of the gelation temperature. Another interesting prediction is the existence, at low volume fractions, of polymer-like “equilibrium polymers”, where the monomers are composed of colloidal particles. Such structures can form through the combination of a deep but short-ranged free energy minimum and a long-ranged repulsion. These interactions tend to cause particles in a cluster to align themselves linearly, as this will reduce the overall repulsion. In other words, we find that highly anisotropic polymer-like structures emerge from association of particles that interact with spherically symmetric interactions!

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# Tube Concept for Entangled Stiff Fibers Predicts Their Dynamics in Space and Time

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Long, stiff filaments are abundant in nature and nano-technology and form entangled meshworks of remarkable mechanical response and complex dynamic behavior [1]. In the semidilute regime the excluded volume becomes irrelevant, such that the filaments in solution diffuse as infinitely thin needles and their peculiar transport properties emerge due to topological constraints imposed by their neighboring impenetrable filaments.

We study such dynamically crowded solutions of infinitely thin needles of length  $L$  for reduced densities  $n^* = nL^3$  deep in the semidilute regime  $n^* \gg 1$ . By computer simulations of needle liquids and needle Lorentz systems where a tracer needle explores a quenched array of other needles we corroborate the scaling behavior  $n^{*-2}$  of the self-diffusion coefficients for rotation and translation [2, 3, 4].

The dynamics of a needle in space and time is assessed by the intermediate scattering function [5]:

$$F(k, t) = \langle \exp(-i\mathbf{k} \cdot \Delta\mathbf{r}(t)) \rangle, \quad (1)$$

with wave vector  $\mathbf{k}$  and the displacement  $\Delta\mathbf{r}(t)$  of the geometric center of the needle in lag time  $t$ . We find excellent agreement between the intermediate scattering function in the semidilute regime and a full analytic solution for a freely moving needle in terms of spheroidal wave functions with transport coefficients obtained from the computer simulation as input parameters [6, 7].

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## Chirality-mediated interaction between knots on tensioned polymers

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Knots appear frequently in semiflexible (bio)polymers, including double-stranded DNA, and their presence can affect the polymers' physical and functional properties. It is possible and indeed often the case that multiple knots appear on a single chain, with effects which are under scrutiny since only a few years. In this talk I will discuss the equilibrium properties of two knots on a stretched semiflexible polymer, an idealization of a typical optical tweezer experiment. Specifically, I will focus on how the knots' relative chirality affects their interaction, rationalizing some of their pertinent features by means of simple effective models. The implications of the chirality-dependent knot-knot interaction will be discussed, in particular with respect to their consequences for the characterization and manipulation of these systems -be they artificial or of biological origin- and for their technological application.

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## Non-monotonous polymer translocation time across porous media: an analytical/numerical perspective

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Understanding the dynamics of polymers in crowded environments and heterogeneous media is of primary relevance due to its biological as well as technological applications. In this view, much attention has been paid to the problem of the translocation of polymers across small pores from both experimental as well theoretical perspectives [1]. However, up to now, the attention of many groups have focused on the case in which polymers translocate across pores whose size is comparable to the size of their monomers. In this contribution we discuss an alternative scenario, namely the case in which polymers move in a porous medium whose smallest pores are larger than the size of the monomers, yet the pores are comparable to the radius of gyration of the polymers. We show that, in such a scenario, novel dynamical regimes appear. In particular, the time polymers take to translocate across the pore has a non-monotonous dependence on polymers length for which shorter polymers experience longer translocation times as compared to longer ones [2]. Accordingly, in such a regime, the maximum translocation time is obtained for a finite-length polymer. In order to understand the physics of such a behavior, we compare numerical results with a simplified model that accounts for the dynamics of the center of mass of the polymer via an effective potential derived from the equilibrium free energy of a polymer confined between parallel plates. Interestingly, despite its simplicity, the model has a remarkably good quantitative agreement with Brownian Dynamics simulations of both Gaussian and self-avoiding polymers. Moreover, the model identifies the relevant dimensionless parameters controlling polymer translocation time and it provides scaling functions that predict the dependence of the maximum polymer translocation time on the diverse parameters. Finally, we show that the scaling functions can be used to design devices capable to separate polymer by exploiting the non-monotonous dependence of polymer translocation time on their size.

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## Diffusion of a protein: the role of fluctuation-induced hydrodynamic coupling

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Proteins and enzymes are able to perform highly precise functions in conditions dominated by thermal fluctuations and viscous hydrodynamics. They typically convert chemical energy into mechanical work, and these nonequilibrium transformations are usually associated with structural modifications. Therefore, the role of the chemical activity of proteins and enzymes, and more precisely of their conformational fluctuations on their transport and diffusion properties is a key problem of biophysics. In particular, recent experimental studies have shown how the diffusion coefficient of enzymes was affected by their catalytic activity [1, 2]. In order to get a better insight in the physical mechanisms at stake in these phenomena, we study a simple model for an enzyme or for a generic macromolecular complex. The modular structure of the molecule is represented by an asymmetric dumbbell made of two hydrodynamically coupled subunits [3]. A detailed analytical study of the stochastic dynamics of the system reveals that equilibrium fluctuations can lead to an interplay between the internal and the external degrees of freedom and give rise to negative contributions to the overall diffusion coefficient. These fluctuation-induced contributions are controlled by the strength of the interactions between the subunits and their geometric characteristics. We also propose a simplified picture that unveils the effect of the chemical activity on the fluctuations of the position of this model macromolecule.

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## Confinement effects in biopolymer thin films

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Chitosan, a biopolymer derived from the second most abundant polysaccharide in nature “chitin”, is a linear polymer of  $\alpha(1\rightarrow4)$ -linked 2-amino-2-deoxy- $\beta$ -D-glucopyranose [1, 2]. It has wide range of applications in the cutting-edge technology owing to its biocompatibility, biodegradability and presence of multi-functional groups on its backbone [2]. In this work, effects of confinement on the structure, characteristic temperature ( $T_c$ ) and swelling kinetics of thin chitosan films with thickness ranging from 6 nm to 270 nm will be investigated. X-ray Reflectivity (XRR) and Spectroscopic Ellipsometry (SE) techniques are employed to measure the physical properties and swelling kinetics of the biopolymer thin films. The mass density of the biopolymer films was extracted from critical wave vector obtained from XRR and was found to increase with decrease in film thickness. Moreover, temperature variation SE measurements reveal a significant decrease in  $T_c$  upon reduction in the film thickness. In addition, swelling kinetics of the chitosan thin films were found to decrease with decrease in film thickness. The evolution of  $T_c$ , densification, and swelling kinetics as a function of degree of confinement will be presented in detail [3].

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We perform extensive molecular dynamics simulations of a strongly charged polymer in a dilute salt free solution in the regime where the chain is collapsed. We identify a series of sub-regimes inside the collapsed regime phase, characterized by different exponents in the scaling relation for radius of gyration,  $R_g \sim \ell_B^{-\gamma}$ , where  $\ell_B$  is the reduced Bjerrum length. To explain the observed results, we develop a new theory based on the counterion fluctuation theory [1] by including appropriate volume interactions between chain monomers as well as between the chain monomers and counterions. We get a general expression for  $\gamma = 1/(3k-4)$  for the  $k^{\text{th}}$  volume term. The new theory consistently describes the observed collapse regimes irrespective of the solvent quality and valency of counterions. Our MD simulations, for both good [2] and poor solvent [3], support the modified counterion fluctuation theory.

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## A coarse-grained dsDNA model optimized for electrokinetic applications

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We present a coarse-grained (CG) model of a charged double-stranded (ds) DNA immersed in an electrolyte solution that can be used for a variety of electrokinetic applications involving dsDNA. The approach is based on an earlier rigid and immobile model of Weik et al. [1] and includes now semi-flexibility and mobility, so that dsDNA dynamics can be sufficiently captured to simulate a full nanopore translocation process. To this end we couple the DNA hydrodynamically via a raspberry approach to a lattice-Boltzmann fluid and parametrize the counterions with a distant dependent friction term. The electrokinetic properties of the DNA model inside an infinite cylinder is fitted against experimental and all-atom simulation data [2, 3]. The stiffness of our dsDNA is tuned with the help of a harmonic angle potential and fitted against experimental data of Brunet et al. [4]. Finally, the quality of our parameter set is tested by measuring the electrophoretic mobility of our CG dsDNA model for various numbers of base-pairs and salt concentrations. Our results compare excellently with the experimental data sets of Stellwagen et al. [5, 6] and Hoagland et al. [7].

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## Bayesian optimization of coarse-grain molecular models by statistical trajectory matching

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Simulations of the molecular dynamics (MD) of complex liquids with atomic resolution can yield relatively accurate results. However, when dynamics is slow (polymers, ionic liquids, ...) or for big systems (micelles), the computational cost rapidly becomes prohibitive. Coarse-grained (CG) models are an appealing alternative: by reducing the number of degrees of freedom and increasing the simulation time step, they allow for simulating bigger systems on longer times. The challenge is thus to develop as faithful coarse grained representations of the atomic systems as possible, regarding static and dynamic properties.

The eliminated degrees of freedom can be taken into account using random and dissipative interactions. We introduce a new method [1] for parameterizing dissipative CG models by maximizing the likelihood to reproduce a high resolution reference MD trajectory. The method yields both conservative *and* dissipative model parameters. A practical, analytical expression of the optimal parameters can be obtained for simple CG models. Single-bead liquid pentane was used as a test case. Simulations of the optimized CG model show a very good agreement with the reference regarding structure (RDFs) and dynamics (self-diffusion).

Extensions of the method allow for including box dimensions and/or tilt as dynamical degrees of freedom (NPT ensemble) and for combining reference trajectories at multiple temperatures/pressures. Liquid vapor equilibria of pentane have been simulated with good agreement regarding liquid density, vapor pressure and surface tension over more than 200 K up to the critical point [2]. On the other hand, dynamic properties sometimes deviate significantly from the all-atom reference when complex interactions are present (associative systems).

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## Modeling of Polyelectrolyte Adsorption from Micellar Solutions onto Biomimetic Substrates

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Depositing cationic polyelectrolytes (PEs), from micellar solutions that include surfactants (SU) onto surfaces is a rich, complex, highly relevant and challenging topic that covers a broad field of practical applications, *e.g.* from industrial to personal care. The role of the molecular architecture of the constituents of the PEs are often overruled, or at least and either, underestimated in regard to the surface properties. In this work, we aim to evaluate the effect of a model bio-mimetic surface, that shares the key characteristics of the extreme surface of hair and its concomitant chemo- and physi-sorbed properties, onto the deposition of a complex PEs:SU system. To tackle out the effect of the molecular architecture of the PEs, we consider *(i)*, a purely linear and hydrophilic PE ( $P_{100}$ ) and *(ii)*, a PE with lateral amphiphilic chains (PegPE) [1]. Using numerical Self-Consistent Field calculations, we show that the architecture of the constituents interfere with the surface properties in a non-intuitive way such that, depending on the amphiphilicity and hydrophilicity of the PEs and the hydrophobicity of the surface, a re-entrant adsorbing transition can be observed, the lipid coverage of the model hair surface being the unique control parameter. Such a behavior is rationalized by the anti-cooperative associative properties of the coacervate micelles in solution, which is also controlled by the architecture of the PEs and SU [2]. We now expect that PEs adsorption, as a rule, is governed by the molecular details of the species in solution as well as the surface specificities. We emphasize that molecular realistic modeling is essential to rationalize and optimize adsorption process of, *e.g.* polymer conditioning agents in water-rinsed cosmetic or textile applications.

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## Hydration Effects Turn a Highly Stretched Polymer from an Entropic into an Energetic Spring

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Polyethylene glycol (PEG) is a structurally simple and nontoxic water-soluble polymer that is widely used in medical and pharmaceutical applications as molecular linker and spacer. In such applications, PEG's elastic response against conformational deformations is key to its function. According to text-book knowledge, a polymer reacts to the stretching of its end-to-end separation by a decrease in entropy that is due to the reduction of available conformations, which is why polymers are commonly called entropic springs. By a combination of single-molecule force spectroscopy experiments with molecular dynamics simulations in explicit water, we show that entropic hydration effects almost exactly compensate the chain conformational entropy loss at high stretching. Our simulations reveal that this entropic compensation is due to the stretching-induced release of water molecules that in the relaxed state form double hydrogen bonds with PEG. As a consequence, the stretching response of PEG is predominantly of energetic, not of entropic, origin at high forces and caused by hydration effects, while PEG backbone deformations only play a minor role. These findings demonstrate the importance of hydration for the mechanics of macromolecules and constitute a case example that sheds light on the antagonistic interplay of conformational and hydration degrees of freedom [1].

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## Local pH of linear weak polyelectrolytes

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Non-ideal titration behaviour of weak polyelectrolytes points to considerable differences between local and bulk pH. We studied the influence of polymer chain length, polymer concentration and solvent permittivity on ionization of linear weak polyelectrolytes. We encountered significant shifts and deformations of respective titration curves. We explain the observed differences between local and bulk pH by means of counterion condensation and ion correlation effects. [1].

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## Droplet model to investigate watermark defects in immersion lithography

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The prevention of watermark defects is a challenge for the immersion lithography industry. Due to the hydrophobicity of the photoresist layer, a fraction of the immersion water breaks up into droplets, which can have a detrimental effect resulting from permeation into it. To get a grip on what physical parameters determine the behaviour of such droplets, we propose a phenomenological model describing the dynamics of a droplet deposited on a permeable surface. The theory includes a description of the evaporation of the fluid using a macroscopic diffusion-based model, and permeation of it into the photoresist layer using Darcy's law. Our theory hinges on relaxational dynamics in a free energy landscape, in this case dominated by surface free energies. It reproduces known contact angle relaxation dynamics after droplet deposition, and provides predictions for the time evolution of the volume and shape of the droplet subject to evaporation and permeation. We study the redistribution of photoresist constituents by means of diffusion from the photoresist layer into the droplet and back, and the impact of contact line pinning caused by precipitation when the solubility limit of the constituents is reached. The redistribution of constituents in the photoresist show qualitative similarities to experimentally measured watermark defects.

## Mechanical properties of bimodal gels under tension

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Most conventional polymer gels suffer from low mechanical strength and toughness, which may limit their practical use, for example in applications where load bearing is required. Designing materials that mimic the unique characteristics of soft biological components is of crucial importance in, *e.g.*, biomedical applications, such as the replacement or engineering of load-bearing tissues. It is also an ongoing challenge, in particular in applications where a combination of seemingly contradictory properties are required, *e.g.*, high toughness for load bearing and high stiffness, combined with stretchability. Furthermore, understanding the toughening mechanism may provide a framework for the future design of materials that fulfil the application demands. For this purpose, it is necessary to be able to correlate the mechanical properties with the network structure to obtain insight into which factors give rise to the desired properties. This task is complicated by the presence of structural defects, such as dangling chains, loops, and entanglements, as well as a spatially inhomogeneous cross-linking density. Computer simulations are advantageous by providing a means of controlling the molecular structure. Decoupling the various structural factors allows for a systematic analysis of the different contributions to the mechanical properties.

One approach for enhancing the mechanical properties of a network is to use a bimodal molecular weight distribution. At certain compositions of short and long chains, these systems display greater strength and toughness compared to their constituent unimodal networks, while maintaining a high value of stretchability. Different theories have been proposed to explain the superior properties arising from bimodality; the two main suppositions have been the limited extensibility of the short chains at larger strains due to a reapportioning of strain and the presence of inhomogeneities within the network structure.

Here, we investigate the relationship between the topology and the tensile properties of defect-free cross-linked bimodal gels with well-defined structures, by means of computer simulations. The deformation behaviour and fracture are studied by imposing a uniaxial strain on networks with varying compositions and chain lengths. We also explore the structural component of the toughening mechanism for systems ranging from perfectly homogeneous to purposely heterogeneous networks with local highly cross-linked clusters of various sizes and compare with those of the constituent unimodal networks.



## Molecular simulations of functionalised copolymers in bulk and in confinement: uncovering the role of functional-group distribution

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Organic additives in oil-based lubricants are used to reduce friction, reduce wear, reduce oxidation, increase performance, improve viscosity index, and even control the way the oil degrades. With such an important role being played by the additives, it is imperative that the physical mechanisms of action are understood, so that better, more efficient lubricants can be developed. This work is focused on atomistic molecular dynamics (MD) simulations of polymeric additives possessing different distributions of polar functional groups (FGs) attached to a polyethylene-polypropylene copolymer backbone. The functionalised polymers are immersed in a non-polar solvent, either in bulk or in confinement between parallel iron oxide walls. The MD simulations reveal that the size of the polymer – as measured by the radius of gyration  $R_g$  – is very sensitive to the distribution of FGs on the backbone. This is shown to be due to the association of the FGs, and the detailed atomistic interactions responsible for this are elucidated. In addition, predictions highlight of the form factor,  $P(q)$ , can be tested against results from small-angle neutron scattering experiments. Similarly, MD simulations of confined polymer solutions point towards a link between the functional-group distribution and the adsorption of the polymers on to inorganic surfaces. Some links between all of these properties and the tribological effects of functionalised copolymers are put forward.

## Universal shape properties of mesoscopic polymer chains, polymer stars and their aggregates

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We analyse the shape characteristics of various macromolecules dissolved in a solvent. Both solute and solvent are considered on a coarse-grained level via the dissipative particle dynamics simulations, thus reducing the effects of chemical content down to the level of solvophobicity of the individual polymer fragments. In the case study A we discuss a linear chain in a good solvent in the infinite dilution regime [1]. At this level of detailisation, its properties depend exclusively on the space dimension  $d$ . The results obtained for the mean prolateness, asphericity and size ratio at  $d = 3$  are in a good agreement with available analytic and MC simulation data and give an evidence of the universality of the shape of the coarse-grained polymer coil in a good solvent. We also discuss the probability distributions for the same set of shape characteristics. In the case study B we extend our analysis to the cases of homo-star (has been considered earlier) and hetero-star (considered for the first time here) polymers and to the case of a solvent of variable quality. The hetero-star molecule is characterised by different solvophobicity of its individual arms. We found an interesting effect that, upon the change of the solvent properties, the asphericity of a homo-star reaches its maximum value when the solvent is at the  $\theta$ -point condition. The effect is explained by the interplay of the enthalpic and entropic contributions to the free energy. In the case study C we consider aggregation of the amphiphilic stars in a solvent [2]. Four different architectures of the same molecular weight and composition are examined, namely: the miktoarm star, two different diblock stars and a set of four disjoint linear diblock copolymers. The shape of the aggregate is examined depending on the aggregation number  $N_a$ . In total, four different shape types are observed: spherical, rod-like and disc-like micelle and a spherical vesicle. Upon the increase of  $N_a$ , a continuous transition from the spherical to a non-spherical micelle is observed first, followed by a discontinuous transition of a non-spherical micelle into a spherical vesicle. Both transitions are discussed in terms of various free-energy contributions.

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## Inhibition of self-replication of protein fibrils

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The formation of nanoscale linear filaments is a ubiquitous form of protein self-assembly. A number of intricate processes simultaneously participate in the formation of filaments including nucleation, elongation, fragmentation and self-replication. The later in particular has emerged as a general feature of pathological protein self-assembly, observed in the context of many medical disorders such as Alzheimer's disease, type II diabetes, Parkinson's disease, and sickle cell anemia.

By comparing experimental data from aggregation of Alzheimer's  $A\beta$  peptide and results from computer simulations we recently established that a key physical determinant governing autocatalytic replication of fibrils is the surface coverage of fibrils by monomeric proteins [2]. In this study we ask the general question about the fundamental ingredients of molecules that can inhibit filament self-replication. To this end, we introduce inhibitor molecules that can compete for the fibril surface with monomeric proteins. We find that: 1) indeed, both in experiments of  $A\beta$  aggregation and in our computer model[2, 3], introducing inhibitors reduces the surface coverage of the fibrils which correspondingly drives down the rate of self-replication. 2) Bound inhibitors not only deplete the surface available for monomer binding, but at the same time drive cluster formation of monomers on the fibril via volume exclusion, a clear manifestation of a crowding effect. 3) As a result, average monomer cluster size on the fibril, not monomer surface coverage itself, uniquely determines the rate of self-replication in the presence of inhibitors.

As self-replication of amyloid fibrils is a major source of potentially toxic oligomers implicated in amyloidogenic diseases, these results can contribute to rational circumvention of species central to amyloidogenic pathologies.

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## Improving the coupling between Molecular Dynamics and Lattice Boltzmann

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We consider the dissipative coupling between a stochastic Lattice Boltzmann (LB) fluid and a particle-based Molecular Dynamics (MD) system, as it was first introduced by Ahlrichs and Dünweg[1]. The fluid velocity at the position of a particle is determined by interpolation, such that a Stokes friction force gives rise to an exchange of momentum between the particle and the surrounding fluid nodes. For efficiency reasons, the LB time step is chosen as a multiple of the MD time step, such that the MD system is updated more frequently than the LB fluid. In this situation, there are different ways to implement the coupling: Either the fluid velocity at the surrounding nodes is only updated every LB time step, or it is updated every MD step. It is demonstrated that the latter choice, which enforces momentum conservation on a significantly shorter time scale, is clearly superior in terms of temperature stability and accuracy, and nevertheless only marginally slower in terms of execution speed. The second variant is therefore the recommended implementation.

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## Scalable and fast heterogeneous molecular simulation with predictive parallelization schemes

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Multiscale and inhomogeneous molecular systems are challenging topics in the field of molecular simulation. In particular, modeling biological systems in the context of multiscale simulations and exploring material properties are driving a permanent development of new simulation methods and optimizing algorithms. In computational terms, those methods require parallelization schemes that make a productive use of computational resources for each simulation and from its genesis. Here, we introduce the heterogeneous domain decomposition algorithm which is a combination of a heterogeneity sensitive spatial domain decomposition with an *a priori* sliding subdomain-walls procedure. The algorithm modeling is presented for dual resolution systems and inhomogeneous binary fluids, in terms of scaling properties as a function of the size of the low-resolution region and the high to low resolutions ratio. We also show the algorithm competences, by comparing it to its initial domain decomposition algorithms and dynamic load balancing schemes. Specifically, two representative molecular systems have been simulated and compared to the heterogeneous domain decomposition proposed in this work. These two systems comprise an adaptive resolution simulation of a biomolecule solvated in water and a phase separated binary Lennard-Jones fluid.

# **Topic 5**

## **Colloids**

## Ferromagnetic phases in colloidal suspensions

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A ferromagnetic phase of anisotropic particles suspended in a nematic liquid crystal (NLC) was predicted as early as 1970 [1]. A recent experimental realization [2] confirmed that a dilute suspension of magnetic platelets in NLC forms ferromagnetic phase which is susceptible to weak magnetic fields. In this work we describe such a suspension of plate-like particles using density functional theory. The influence of the NLC is taken into account implicitly through the introduction of the effective elastic interaction between platelets. Following approach of Lev and Tomchuk [3], the effective potential was derived under the assumption of weak anchoring of the NLC at the surface of the platelets. An ordered phase was identified with help of the orientational distribution function, and the dependence of the ferromagnetic phase on the strength of the magnetic and the elastic coupling was studied.

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Hierarchical self-assembly, which involves more than one self-assembly step, is a strategy used by nature to accurately build complex micro-structures. Although it is widely believed that hierarchical self-assembling strategy may be the most efficient one, no theoretical work directly proves this idea. In this work, we study one of the simplest hierarchical self-assembly system i.e. two hemispheres (primary building blocks) first self-assemble into one hard sphere through dimerization. Then the structured hard spheres, acting as a secondary building block, further self-assemble into FCC crystal. By adjusting the dimerization strength, a gradual transformation from a rigorous two-step hierarchical self-assembling (hemisphere-> sphere-> FCC crystal) to a non-hierarchical one-step process (hemisphere -> FCC crystal) can be achieved. We find that, at the same super-saturation condition, the nucleation barrier increases dramatically as the fraction of primary building block increases. The reason behind this phenomenon is that, comparing with secondary building block, primary building blocks are less compatible with the final crystal interface. Detailed analyses reveal that there is a large portion of liquid hemispheres attaching on the solid interface with wrong orientation. Despite the loss of most orientation entropy, these erroneously oriented hemispheres cannot gain additional translation entropy in the same way that the solid hemispheres do. This raises the interface free energy and heightens the nucleation barriers. Moreover, the “self-poisoning” during the crystal grow and the suppression of the crystal grow rate are also observed as the concentration of primary building blocks increases. Based on this minimal model, our work provides direct evidences that in complex self-assembly process, a rigorous hierarchy is necessary to obtain a large-scale and error-free self-assembled structure.



## Colloidal suspensions in one-phase mixed solvents under shear flow

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We numerically study behaviors of colloidal suspensions in one-phase mixed solvents under shear flows. Far from the phase separation point, the colloid particles are dispersed well and the suspension shows a Newtonian viscosity. When the mixture is brought near the coexistence curve, the colloidal particles are aggregated by attractive interactions due to the concentration heterogeneity caused by the surface wetting. This aggregating interaction is enhanced when the component favored by the colloidal surface is poor. We found its viscosity is increased with approaching to the phase separation point. Near the coexistence curve the suspension shows a shear thinning behavior, since the aggregated structure is rearranged into small clusters under the shear flow. Our simulations also suggest that the shear flow does not change the concentration profiles around the particles so importantly at the onset of the rearrangement of the aggregates. Thus, we can consider that the effective interaction is almost free from the shear flow and remains isotropic.

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Self-assembly of stably trapped colloidal particles at electrolyte interfaces has attracted much interest in recent years. For charge stabilized colloids at the interface, the attractive part of the interaction is dominated by strong van der Waals force which is balanced by a repulsive part coming from the electrostatic repulsion between the colloids. For large separations between the particles, this repulsive part of the interaction can be compared to a dipole-dipole interaction. However for distances close to the particle this simple dipolar picture cannot be applied. In this contribution, the effective electrostatic interaction between a pair of colloids, located close to each other (inter-particle separation small compared to the size of the particles) at an electrolyte interface, will be discussed by employing the full, nonlinear Poisson-Boltzmann (PB) theory within classical density functional theory. Using a simplified yet appropriate model, all contributions to the effective interaction are obtained exactly, albeit numerically. The comparison between our results [1] and those obtained within linearized PB theory [2] reveals that the latter overestimates these contributions significantly at short inter-particle separations. Whereas the surface contributions to the linear and the nonlinear PB results differ only quantitatively, the line contributions show qualitative differences at short separations. Moreover, a dependence of the line contribution on the solvation properties of the two adjacent liquids is found, which is absent within the linear theory. Our results are expected to enrich the understanding of effective interfacial interactions between colloids.

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## Model-dependent phase behavior of hard and soft particle mixtures.

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We use integral equation theory and computer simulations to describe the equilibrium structure and phase behavior of hard and penetrable particle mixtures. Previous studies have shown that a system of purely penetrable particles can show reentrant melting behavior (Gaussian core model [1]) as well as a cluster crystalline phase (generalized exponential model [2]), depending on the stiffness of the soft bounded repulsive potential. We find that introducing a modest amount of hard particles destroys the cluster crystals. Instead, depending on the fraction of hard particles the homogeneous fluid may undergo a macrophase separation or a microphase separation as the density increases. The latter, results in locally segregated hard-rich and soft-rich domains. Depending on the total density of the system, solid-like ordering may be present within these domains. Moreover, the kinds of microphase ordered structures formed are a function of the stiffness of the soft bounded potentials. Curiously, we also find a relationship between the cross interactions between hard and soft particles and the presence or absence of microphase order.

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## Colloidal grain boundary loops: creation, shrinkage, and condition of existence

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Understanding the structure and dynamics of grain boundaries is key to unravel the properties of polycrystalline materials. In two-dimensional materials, grain boundaries merely consist of lines of topological defects, termed dislocations, and form a network. When the line closes onto itself, a grain boundary loop is formed, which encloses a portion of crystal rotated by some angle called the misorientation. While grain boundary loops feature in several scenarios of stress relaxation and topological phase transitions, their structure and dynamics remain largely unexplored in a systematic manner.

Here, we create grain boundary loops on demand by deforming two-dimensional colloidal crystals with optical vortices. We find that they spontaneously shrink due to capillary forces at a rate that solely depends on the product of their radius and misorientation. We show that for a grain boundary loop to exist following the deformation, the product of its radius and misorientation has to be greater than a critical value, due to the confinement of the dislocations on the loop. This critical value is reached by grain boundary loops that have the same dislocation structure as the so called “flower defect”, which is encountered in graphene. Our results thus reveal a general limit on the formation of grain boundary loops following deformation or melting of 2D hexagonal crystals.

## Direct observation of dislocation and particle dynamics during grain boundary migration

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Grain boundaries can migrate over distances large enough to induce major structural changes in polycrystalline materials. It is clear that at the microscopic level, grain boundary motion originates from the displacements and rearrangements of atoms, enabling the conversion of one crystal into the other. Grain boundary migration can also be considered from a topological point of view, as it is achieved by the motion and reactions of dislocations. However, both mechanisms and their link remain unclear, due to limitations of current atomic imaging techniques.

Here, we uncover the microscopic mechanisms of grain boundary migration in circular colloidal grain boundaries –grain boundary loops – created using optical vortices. The grain boundary loops are topologically well defined owing to their zero net Burgers vector and undergo spontaneous capillary-driven migration and shrinkage until complete annihilation. We directly visualise the dislocation dynamics and reactions involved, and show that they lead to strong dynamical heterogeneities among the particles swept by the grain boundary. In particular, we analyse the displacements of particles that allow for the motion of dislocations. Finally, we reveal the remarkable link between the grain boundary structure and dynamical heterogeneities for the case of coincident site lattice boundaries.

## Liquid-state approaches to protein solutions: from protein phase behaviour to the second virial coefficient

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We experimentally determined the phase behaviour and the interactions of protein (lysozyme) solutions under conditions favouring protein crystallization and metastable gas-liquid phase separation [1-3]. The phase behaviour as well as the interactions show striking similarities to those of colloids with short-ranged attractions. In particular, we find that the rescaled metastable gas-liquid binodals of protein solutions can be mapped onto those of square-well fluids [4]. Despite their much more complex interactions, protein solutions hence appear to also follow the extended law of corresponding states [5].

Moreover, we exploit this extended law of corresponding states and apply the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory in order to infer the second virial coefficient  $B_2$  from the phase behaviour, namely, the cloud-point temperature (CPT) [6]. This determination of  $B_2$  yields values that quantitatively agree with results of static light scattering (SLS) experiments. Within this approach, the strength of the attractions is quantified in terms of an effective Hamaker constant, which accounts for van der Waals attractions as well as non-DLVO forces, such as hydration and hydrophobic interactions. This approach is based on simple lab experiments to determine the CPT and combined with the DLVO theory. Due to this simplicity, it can be applied to a wide range of protein-protein interactions including complex solution environments. This is expected to facilitate further biophysical research.

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# Electrophoretic mobility of low salt aqueous charged sphere suspensions

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The mobility of low salt aqueous suspensions of charged colloidal spheres has been investigated for a long time. There exists a qualitative discrepancy in the observations made on its particle number density dependence [1-7]. Some authors observed the theoretically expected decrease, but others consistently reported an unexpected and still unexplained increase of the electrophoretic mobility with increasing particle number density. In this paper, we report preliminary data measured over a wide range of densities from highly dilute to very concentrated systems, already showing strong multiple scattering. We perform super-heterodyne Doppler velocimetry in a low angle reference beam configuration. We apply an empirical correction scheme to correct for the multiple scattering contribution and extract the desired mobility data from fits of theoretical expressions to the single scattering Doppler spectra. We observe an increase of mobility, followed by a plateau and finally a decrease. Our observations indicate the possibility to reconcile previously published data and furthermore present a severe challenge to electrophoretic theory, which does not foresee any increase in mobility with particle number density.

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## Dramatic influence of anisotropic interactions on short time diffusion and arrest of protein solutions

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In a dense and crowded environment such as the cell, an individual protein feels the presence of surrounding proteins. It is thus expected that direct and hydrodynamic interactions strongly affect the diffusion of proteins. Examples are suspensions of eye lens proteins, where a dramatic slow down of the local short time diffusion of  $\gamma_B$ -crystallin and a dynamical arrest is observed experimentally under crowded conditions [1]. Here, we demonstrate that an application of colloid models, together with appropriate theoretical and simulation tools that allow to incorporate direct and hydrodynamic interactions, provides detailed insight into the dynamics of protein solutions. The hybrid simulation approach combines the multiparticle collision dynamics (MPC) method for the fluid with molecular dynamics simulations (MD) for the globular proteins [2]. We present results for the short time diffusion of different model proteins, where their dynamics are analyzed together with structural properties. The effect of hydrodynamic interactions as well as anisotropic attractions between colloids are discussed. In particular, we highlight the dramatic effect of weak attractive interactions known to exist between many globular proteins on the short time diffusion under crowded conditions, and compare this with the location of the arrest line. We point out that short time diffusion provides important insight into the different mechanisms responsible for the formation of an arrested glass at high protein concentrations.

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## Double layer structure of topological colloids

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The topology of colloidal particles with a non-trivial shape can couple strongly to the medium in which they reside. For example, when the medium is a liquid crystal, topological defects form in the medium that couple strongly to the topology of the particle shape [1,2], which, in turn, can be used to form colloidal crystals that are stabilized by topological binding [3]. However, up until now only uncharged particles are considered, and no attention has been paid to topological charged particles and their coupling to a medium with ions. This coupling leads to the formation of an electric double layer [4], that consists of the charge distribution of the particle and a diffuse ionic layer that screens the particle charge. We will carefully investigate the topology of the double layer in terms of the electric field, particle charge distribution, and the ion density distributions, and we will show that the double layer topology strongly depends on salt concentration and particle geometry.

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# Crowding and interaction effects in multi-component diffusion-controlled reactions

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Diffusion-controlled reactions are typically described within the Smoluchowski approach [1], which neglects interparticle interactions. In these systems, a reactant diffuses towards a catalytic particle and, after interacting with the particle surface, gives rise to a product which diffuses away from the catalyst. We propose a simple way to incorporate crowding and interaction effects between reactants and products by including the osmotic pressure and hydrodynamic interactions of the nonideal particles in the Smoluchowski equation within a local-density approximation [2,3,4]. We solve numerically the strictly linearized equation for the time-independent case with absorbing boundary conditions, and analyze the spatial distribution of reactants and products and the steady-state rate constant for moderate catalyst concentrations. Our analysis is made in terms of second virial coefficients  $B_2$  for the reactant-reactant, product-product, and reactant-product interactions. We assess the validity of our results by means of Brownian dynamics simulations excluding hydrodynamic interactions. We find that the inclusion of attractive (repulsive) interactions between reactants and products substantially increases (decreases) the reaction rate.

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Thermoresponsive colloidal microgels have shown to form elastic, amorphous networks upon raising the temperature. Through their thermosensitivity, either soft repulsive or hard attractive colloidal systems can be obtained, and switched reversibly and in situ by a small temperature change [1]. Switching the system from repulsive to attractive particles allows for elastic network formation that can be manipulated easily with several parameters, such as volume fraction, salinity or temperature gradient [2].

Extending this approach to binary microgel mixtures that collapse at different temperatures yields novel nonequilibrium structures with new structural and mechanical properties [3]. Collapsing the two particles sequentially offers for example the possibility of obtaining a decorated network. The kinetics with which this formation and decoration occurs are crucial, and we analyze these using a combination of experimental techniques and simulation. We have developed a coarse-grained model that allows us to simulate the temperature dependence of the potential and follow the time-resolved structural aging, which we compare to in situ confocal microscopy imaging. Additionally, we will discuss the effects of the kinetics on the macroscopic elasticity, as well as the effects of the microscopic mobility.

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## Dynamic assembly of magnetic colloidal vortices

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Magnetic colloids in external time-dependent fields are subject to complex induced many-body interactions governing their self-assembly into a variety of equilibrium and out-of-equilibrium structures such as chains, networks, suspended membranes, and colloidal foams. Here [1], we report experiments, simulations and theory probing the dynamic assembly of superparamagnetic colloids in precessing external magnetic fields. Within a range of field frequencies, we observe dynamic large-scale structures such as ordered phases composed of precessing chains, ribbons or rotating fluidic vortices. We show that the structure formation is inherently coupled to the build-up of torque, which originates from transient correlations among the particles due to internal relaxation of the induced dipoles and short-lived chain formation. We discuss in detail the physical properties of the vortex phase and demonstrate its potential in particle-coating applications.

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## Freezing monolayers of colloidal particles in water

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When freezing the solvent of a colloidal suspension, the colloidal particles may either segregate from the solidifying solid or be engulfed by it, depending on the freezing conditions. This is important in a wide range of research areas, for example in the behaviour of bacteria or cells in cryopreservation [1], in the freeze-casting of porous ceramics [2], and in the food industry, where fat is trapped by ice in the making of ice-cream [3].

Here, we study a model system of colloidal particles confined to a monolayer in the vicinity of ice-water interface, that is moving under the influence of a temperature gradient. We observe how particles pack in front of the interface by analysing the local hexagonal bond-orientational order parameter. We then examine how the advancing interface velocity, the particle properties (such as surface charge and thermal conductivity) and packing fraction, and the temperature gradient lead to different engulfment phenomena. Finally, we relate these observations to models for particle entrapment, where super-cooling, wetting, and lubrication all play a role.

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# Screw-dislocation handedness driven by growth rate in chiral colloidal self-assemblies

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Spontaneous organization of colloids into highly ordered mesoscopic assemblies is a ubiquitous phenomenon in soft matter and biological systems [1, 2]. Among anisotropic nanoparticles, filamentous *fd* viruses have been considered as a model system because of their high monodispersity in size and their ability to act as chiral building blocks [3, 4].

These properties enable them to self-organize into well-defined mesophases whose phase behavior in terms of structure and dynamics is in quantitative agreement with theories and computer simulations for hard rods [5, 6]. We explore here the self-organization of *fd* rods in presence of attractive interactions induced by non-adsorbing polymers [7, 8]. These mixtures lead to the formation of various colloidal structures such as hexagonal platelets composed of a single layer of aligned rods and a long central defect.

Controlled self-assembly into 2D hexagonal platelets and 1D layered columns is demonstrated to depend on both viral rod and polymer concentrations. An analysis of the platelet structure is performed, emphasizing the existence of intrinsic screw dislocation whose handedness is related to both rod chirality and kinetics of growth. We therefore show how chirality amplification can be driven by growth rate in rod-like particle self-assemblies and we propose a scenario to account for these results.

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## Effective interaction potentials in binary mixtures of thermoresponsive microgels

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Thermosensitive microgels display a rich phase behavior due to their unique soft potential and internal structure. Especially, their thermosensitivity allows us to use temperature as an external control to tune particle size, volume fraction and effective interaction potential *in situ*. Here we study binary mixtures of thermoresponsive microgels, where the soft repulsion of the large microgels is complemented by a depletion attraction induced by the presence of the small microgels. By using these binary mixtures, we ensure that while changing the temperature, the size ratio (and thus the relative range of the depletion attraction) remains constant.

We present a systematic experimental study of the structural correlations between large microgels in the presence of small microgels. Though a quantitative understanding of the effective interactions between microgels is still lacking, previous research has shown that a Hertzian potential describes the effective pair potential between these types of microgels very well [1]. We here demonstrate that the effective interaction potential between large microgels in the presence of small microgels cannot be explained by the sum of a depletion attractive potentials and a Hertzian-type soft repulsive potential. Instead, the experimental results can only be reproduced using a more complex multi-Hertzian effective interaction potential to describe the soft repulsion between microgels. We link this potential to the known core-shell structure of the microgels, and investigate in detail the effects of such a multi-Hertzian potential on the resulting effective interactions and structural correlations using computer simulations. We argue that the discrepancy between the behavior found for the pure microgel system and the binary mixture with an additional depletant arises from the fact that the depletion interaction creates a situation where the large particles not only experience the outer soft shell, but also explore the denser microgel interior. We discuss the effect of the core-shell-like inner structure of the microgels on their effective pair potential, and comment on its importance for an improved understanding of the structural and dynamic properties of ultra-dense particle suspensions.

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## Two dimensional melting of deformable particle systems

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Particles of soft polymeric systems such as star polymers, dendrimers, microgels, and polyelectrolyte stars [1, 2], as well as soft granular particles [3, 4], might deform and shrink when compressed by their neighbors at high densities. In this high density regime the effective two-body interaction potentials commonly adopted to describe these systems break down and must be replaced by a truly many-body interaction. Here we investigate how many-body interactions affect the solid-liquid transition of the two dimensional Vertex model, a popular model of epithelial cell tissues. This model naturally captures the many-body nature of the interaction by relating the energy of each particle to the properties of its Voronoi cell. We show that the solid-liquid transition of the Vertex model is first-order with no hexatic phase, in contrast to the prediction of the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory of two-dimensional melting [5]. We also investigate the nucleation process at the melting point and observe that the liquid nucleus closely relates to the particles with large displacements from their equilibrium lattice positions but do not corresponds to particles with low order or low density. Our results provide insight into the solid-liquid transition in systems with many-body interactions and may shed new light on the mechanism of nucleation process.

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## Two-dimensional non-close-packed nematic colloidal assemblies and their electrical response

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Recently, colloidal dispersion in nematic liquid crystals, so-called nematic colloids, has been intensively been studied as a colloidal system of new type. Since the origin of the interaction between colloids is elastic deformation of orientation of nematic liquid crystal, the interaction is anisotropic and larger than the conventional one. One-, two- and three-dimensional crystalline close-packed assemblies have been reported in nematic colloids [1, 2]. Anisotropic (directional) interaction between nematic colloids makes it possible to build anisotropic non-close-packed colloidal assemblies those cannot be realized in isotropic liquid. Colloidal assemblies with electric responsiveness also can be realized by nematic colloids [1]. In this study, we have built complex and non-close-packed assemblies of dipolar nematic colloids in a homeotropically aligned nematic cell and studied their response to electric field.

We used uniform-sized silica microspheres of 4 $\mu$ m in diameter and dispersed them in a homeotropic aligned 5CB. The surfaces of the particles and the cells were treated to promote homeotropic anchoring of 5CB. Most of the particles exhibit dipolar configuration and their point defects site above or below the particle. The antiparallel dipolar colloids attract each other but the parallel ones repel each other. Thus, we can stably bond the antiparallel dipolar particles and make various colloidal structures artificially by manipulating them with optical tweezers.

Two-dimensional (2D) polygonal colloidal assemblies were made by combining antiparallel dipolar chains. Although the formed colloidal assemblies have empty space in their structure, they keep their shape for long time and we can drag them by laser beam. The 2D non-close-packed assemblies including a honeycomb lattice and a block checker lattice also have been formed in hierarchical way from small clusters.

The electric response of the formed structures also has been studied. For example, the 2D polygonal colloidal assembly shrinks homogenously under an electric field. The shrinkage is reversible and the shrink rate in length attains 25% at 5Vrms. Such large electric response of the assembly enables us to utilize them as optic devices whose structures and optical properties can be controlled by electric field.

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# Investigation of thermo-responsive microgels at flat liquid-liquid interfaces: Connection between microgel softness and monolayer properties

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Microgels are 3D, cross-linked polymer networks, typically spherically shaped and in the size range of 50 nm to 10  $\mu$ m. The network is swollen in a good solvent and adjusts its dimensions, density and related properties according to the environmental conditions. Microgels are highly interfacial active and can be employed as emulsion stabilizers. Their usage bears a significant advantage: The stimuli-responsiveness of the microgels leads to stimuli-responsive emulsions. For example, Monteux *et al.* have shown that *N*-isopropylacrylamide (NiPAM) based microgel-stabilized emulsions have a lower stability when heated to above 40 °C, resulting in phase separation [1].

The properties of microgels as emulsifiers are far from being fully understood. The aim of this study is to elucidate the connection between the microgels temperature-dependent swelling state (i.e. softness) and monolayer properties at liquid-liquid interfaces. Thus, thermo-responsive model systems with equal cross-linker densities were synthesized from NiPAM and *N,N*-Diethylacryl-amide (DEAAM); the incorporation of DEAAM leads to a reduction of the volume phase transition temperature of the microgels. Langmuir compression isotherms were recorded at different temperatures. In accordance with literature two-staged progresses are obtained in swollen state [2]. In contrast, collapsed microgels show only a one-staged progress, similar to rigid particles at liquid-liquid interfaces [3]. The microgels were examined with Freeze-fractured shadow-casting (FreSca) cryo-SEM to obtain information about the protrusion height of the particles into the oil-phase, their interfacial size and morphology as a function of the swelling state [4]. These parameters do not change, and it is expected that the microgel parts situated in the aqueous phase define the monolayer properties. Furthermore, the viscoelastic properties of the monolayers at different temperatures are determined by Interfacial rheology.

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# On the propensity of inverse patchy colloids to self-organize in stable, lamellar structures

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Inverse patchy colloids (IPCs) are mesoscopic particles that are characterized by a heterogeneously charged surface [1]: the charged colloid is decorated by regions of opposite charge (so-called patches). As a consequence of the attraction and the repulsion of the regions of unlike and like charges IPCs are able to form selective and strongly oriented bonds with other particles. As an additional feature, the differently charged regions of IPCs can be addressed by external stimuli, such as electric fields.

We consider in our simulation-based investigations a two-patch model of an IPC: here the patches are located on the poles, leaving the oppositely charged equatorial region uncovered. Via direct pole-equator contacts, interacting IPCs are able to form very strong bonds. This bonding pattern is the basis of the propensity of IPCs to form planar aggregates. The lamellae occur, for instance, as monolayers close to charged substrates [1, 2] or as stacked, parallel layers in bulk equilibrium phases [3], where their range of stability covers a large portion of the parameter space. Recently a novel layered structure has been identified for a particular class of IPCs [4]: it occurs at low temperatures as a stack of parallel layers (each of them characterized by a strong internal bonding pattern), which are stabilized by inter-layer particles that are oriented perpendicularly to the lamellae. As the temperature is increased the system forms an unconventional hybrid crystal-liquid structure: the inter-layer particles have now sufficient energy to become mobile and start to diffuse (as quantified via different dynamic correlation functions) between the layers which still maintain their stable and rigid internal structure. As the temperature is further increased, also the strong intra-layer bonds start to break up and the system eventually melts, realizing thus the second steps in this remarkable two-stage melting process. This (semi-)ordered structure is able to quickly and spontaneously self-organize in simulations (even when starting from a completely random initial configuration) and shows very pronounced self-healing capacities.

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# Formation of Laves Phases in Repulsive and Attractive Hard Sphere Suspensions

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Laves phases (LPs) of  $\text{MgCu}_2$  type are considered to be promising precursors for diamond structure photonic materials [1]. Experimental realizations of LPs have so far been reported for nanoparticles and charged colloidal spheres. Laves phases formed from hard sphere systems of right size and at high packing fraction would greatly improve technical possibilities. We here report on the phase behavior and the crystallization kinetics in a binary mixture of Polystyrene micro-gel based hard sphere approximants of size ratio  $R_S/R_L=0.77$  suspended under excellent buoyancy match in 1-Ethyl-naphtalene. Systems of number ratio  $N_S/N_L=3.2$  were investigated at volume fractions between melting and the glass transition. Analysis of the powder diffraction patterns shows that all phases form LPs of  $\text{MgZn}_2$  structure on the time scale of days to months. Presence of  $\text{MgNi}_2$  structures can safely be excluded.  $\text{MgCu}_2$  structures may be present. These findings are in line with recent theoretical estimates of bulk free energies and corresponding phase diagrams [2]. The same structure is also formed upon the addition of small amounts of non-adsorbing polymer switching the interaction to depletion attractive. Changes in particle volume fraction or polymer concentration, however, strongly affect the crystallization kinetics and resulting crystal quality. We observe a switch from nucleation dominated to growth dominated behavior. In particular for mildly attractive systems, the formation of compacted precursors during nucleation is avoided and high quality crystals can be obtained via accelerated growth. Comparison to previous work from literature further suggests that buoyancy match may play a crucial role in allowing this first observation of LPs in hard sphere suspensions.

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## Colloidal aggregates of tricationic porphyrin on inorganic polyphosphate

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Self-assembled molecular aggregates formed by non-covalent interactions attracts essential attention of scientists due to their unique photophysical properties and potential applications in molecular electronics and nanotechnology including design of new photonic materials and devices, fabrication of light-harvesting systems etc. Self-assembly of *meso*-substituted tris(*N*-methylpyridinium) porphyrin (TMPyP<sup>3+</sup>) in aqueous solution on polyanionic chain of inorganic polyphosphate (PPS) was investigated using techniques of absorption, polarized fluorescence spectroscopy as well as DFT calculation method [1].

Light scattering study has shown that formation of stable colloidal spatially ordered aggregates occurs at phosphate:porphyrin molar ratio of 3.7. From 8-fold fluorescence quenching registered for bound TMPyP<sup>3+</sup> molecules and their Raman spectra it was concluded that porphyrin chromophores form the stable  $\pi$ - $\pi$  stacks onto PPS template. The transformation of the Soret band in the absorption spectra evidences that the assemblies are mixtures of *J*- and *H*-aggregates of porphyrin. Molecular modeling shows that the flexibility of PPS strand allows a realization of spiral or "face-to-face" one-dimensional structures formed by porphyrin molecules arranged in parallel and antiparallel mode. The peculiarity of PPS structure allows a formation of two porphyrin stacks on opposite sides of polymer strands that result in appearance of higher-order aggregates. Their size estimated from the light scattering data reaches several hundred nanometers in diameter. These aggregates are substantially more stable and extended in comparison with those observed earlier for TMPyP4 on the same scaffold and under the similar experimental conditions [2].

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## Sorption and spatial distribution of protein globules in charged hydrogel particles

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Hydrogel nanoparticles are high potential carrier and drug delivery systems for biotechnological and medical applications. However, where in these penetrable systems are the substances actually (ad)sorbed, rather inside or at the surface? In fact, this spatial distribution or 'partitioning' of the drugs inside the carrier is a key factor for the interactions of the carrier-drug complex with its biological environment (due to the presence or absence of a protein 'corona') as well as for the substance uptake and release kinetics. The partitioning is therefore crucial for the functionality of hydrogel particle as drug carrier and delivery systems. In this work, we explore theoretically the partitioning and spatial distribution of a non-uniformly charged biomolecule, suitable to represent a globular protein or a drug, by a charged hydrogel carrier in the presence of a 1:1 electrolyte. Based on the analysis of a recently developed and extended physical interaction Hamiltonian including leading order electrostatic multipolar contributions, we have identified five different sorption states of the system, from complete repulsion of the molecule to its full sorption deep inside the hydrogel, going through meta- and stable surface adsorption states. The results are summarized in state diagrams that also explore the effects of varying the electrolyte concentration, excluded-volume contributions as well as the hydrophobic interaction between protein and hydrogel. We show that the dipole moment of the biomolecule is a key parameter controlling the spatial distribution of the globules. In particular, biomolecules with a large dipole moment tend to be adsorbed at the external surface of the hydrogel, even if like-charged, whereas uniformly charged biomolecules tend to partition towards the internal core of an oppositely charged hydrogel. Our results establish a guidance for the spatial partitioning of proteins and drugs in hydrogel carriers, tuneable by hydrogel charge, pH and salt concentration.

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## Hydrophobically-coated gold nanoparticles: from interaction to superlattices.

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Hydrophobically coated metallic nanoparticles are model systems that are useful to understand the link between interaction and self-assembly. The interactions between these nanoparticles when suspended in oil combine strong attractive van der Waals attraction between the metal cores, interaction between the ligands that depends on solvent conformation [1]. At high concentrations, these nanoparticles spontaneously self-assemble in superlattices when the solvent evaporates. The full phase diagram upon nanoparticles concentration can be established using Ostwald ripening in oil in water emulsions [2].

The final structure, after full evaporation of the solvent, depends on the ratio between the gold core size and the ligand shell thickness. Besides classical FCC or BCC structures, a more complex phase with local tetrahedral packing has been revealed [3]. The existence of such a structure has been analyzed in terms of geometrical parameters including gold core diameter, ligand length, and grafting density and an energetic approach based on van der Waals attraction. This structure is the same as the one recently observed in aqueous suspensions of polydisperse charged particles [4].

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## Diffusion and Arrest of Ellipsoidal Particles in the Presence of an External Field

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Differential dynamic microscopy (DDM) has been recently developed to quantify the dynamics of submicron particles in dispersion from fluctuations of the intensity in optical micrographs [1,2,3]. Although DDM is a powerful technique to measure anisotropic dynamics of concentrated suspensions, its full potential has not been exploited so far. Here we will present the dynamics of anisotropic ellipsoids over a large range of concentrations up to their glass transition using DDM. Prolate colloidal silica-coated hematite particles were used as a model system, and their ability to orient in a homogeneous external magnetic field was exploited to study the combined effects of shape anisotropy and orientation on their diffusion. The angularly resolved diffusion of the particles was measured to determine the particles hydrodynamic dimensions in the dilute regime to validate the technique for our experimental system. Upon increasing the amplitude of the magnetic field, the alignment of the particles perpendicular to the field is promoted, which is manifested by the stronger decoupling of the diffusion parallel and perpendicular to the field which start to diverge at higher concentration. In this presentation, I will primarily focus on the field and concentration dependence of the short- and long-time diffusion coefficient and their connection to the phase behavior of these particles. At zero magnetic field, the long-time diffusion coefficients at higher concentrations decrease dramatically, indicating that the system approaches a glass transition. While the short-time collective diffusion coefficient increases, primarily reflecting the decrease in the static structure factor at low q-values typical for a repulsive system.

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# Phase behaviour and gravity-directed self-assembly of spherical caps

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Using Monte Carlo simulations [1] and free energy calculations [2] we study the phase behaviour of hard spherical caps – spheres of diameter  $\sigma$  cut by a plane at a height  $\chi$ . The geometry of these uniaxial particles is completely defined by the aspect ratio  $\chi^* = \chi/\sigma$  [3]. The spherical cap model is of interest first due to its resemblance to experimental mushroom-cap shaped colloidal particles that have been used for the fabrication of photonic materials [4]. Second, the spherical cap is a non-centrosymmetric shape which approximates a sphere at the limit  $\chi^* = 1$ , allowing for a clear perspective on the effect of particle shape on phase behaviour. We find many stable ordered phases including plastic crystals and dimer-based crystals, though only plastic crystals of low anisotropy are observed to form spontaneously from compression of a bulk isotropic phase. We further study the directed self-assembly of spherical caps via sedimentation onto solid substrates as a method to enhance the formation of several ordered structures. This work shows how a simple gravity field and a template is sufficient to improve the self-assembly of hard anisotropic particles.

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## First passage times in a model membrane channel

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The efficient transportation of particles across membranes is essential to the functioning of a wide range of systems. In nature, this often involves channels or pores which are optimized for transport of a certain species by their size, shape or the inclusion of specific binding sites. Translocation of particles through channels is often characterized by the first passage time as this quantity provides significant insight into details of the channel structure and the rate-limiting steps involved. However, in biological systems it is almost impossible to establish conclusive links between channel structure and particle dynamics since details of the translocation process are often experimentally inaccessible. As such, valuable information is provided by microscale model membrane channels that allow us to study dynamics in detail at the particle level in channels with known structures [1].

Here, we use video microscopy to study the diffusion of colloidal particles in microfluidic channels with internal dimensions close to that of the particle diameter. In particular, we determine the first passage time for particles to escape a channel while subject to fully controlled potential landscapes imposed by holographic optical tweezers. By using the potential energy minima to mimic binding sites, we are thus able to examine in detail translocation through complex energy landscapes and, more specifically, investigate the validity of a simple relationship between the first passage time distribution and the number of binding sites [2].

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## Drying-mediated deposit patterns in dilute colloid-polymer suspensions

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Drying-mediated patterning of colloidal particles is a physical phenomenon that must be understood in inkjet printing technology to obtain crack-free uniform colloidal films [1-4]. Here we experimentally study the drying-mediated patterns of a model colloid-polymer suspension and specifically observe how the deposit pattern appears after droplet evaporation by varying particle size and polymer concentration. We find that at a high polymer concentration, the ringlike pattern appears in suspensions with large colloids, contrary to suppression of ring formation in suspensions with small colloids thanks to colloid-polymer interactions. We attribute this unexpected reversal behavior to hydrodynamics and size dependence of colloid-polymer interactions. This finding would be very useful in developing control of drying-mediated self-assembly to produce crack-free uniform patterns from colloidal fluids.

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## Hard X-ray nanotomography of randomly packed colloidal particles

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Random close packing (RCP) of spheres in three dimensions is important in understanding arrangement and geometry of porous media, metallic glasses, colloids, and granular matter [1-3]. Most theory and analysis are focused on RCP at the large scale [1, 3-4], while actual colloidal particles can exhibit RCP at the nonoscale. Here we show that hard X-ray nanotomography enables us to clearly visualize randomly packed colloidal particles even inside fluids in three dimensions. Particularly, we demonstrate X-ray nanotomographic images for monodisperse colloidal particles with various sizes. We believe that hard X-ray nanotomography would be a powerful tool to identify the nature of colloidal particles inside or on fluids.

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## Microgels in computer simulations

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Colloidal particles, consisting of cross-linked polymers called microgels, are able to swell or shrink as a response to their external environment [1]. The fact that the swelling can be controlled makes microgels promising materials for many applications.

However, the system behavior can be drastically changed by embedding magnetic particles into the system as it is demonstrated in the recent works on the novel magnetic dipolar materials like magnetic gels, brushes and filaments [2,3,4].

In this work, we study the behavior of both nonmagnetic and magnetic microgels. The latter are obtained by embedding magnetic dipolar particles in cross-linked polymers comprising microgels. We elucidate how dipolar interactions alter structural and elastic behavior of microgels. To this aim, we employ Molecular Dynamics simulations where all microgels initially have a spherical shape and observe how the strength of electrostatic interactions and dipole-dipole interactions influence these systems changing the size of microgels and their polymer conformations. We show that embedding magnetic particles in microgels gives us an additional tool to manipulate their swelling along with changing the solvent of the system.

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## Exploring a new class of effective interactions in crowded environment

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Effective interactions play an important role in the physics of colloidal dispersions. The most established way to tune effective potentials is by means of depletion[1]. More recently, effective forces modified by the spontaneous self-assembly of the co-solute have been studied, with critical Casimir-like forces being a famous example[2,3].

In this talk, we examine the effective forces generated by a co-solute which reversibly self-organizes into linear chains or larger aggregates. We use 3D Monte Carlo simulations to calculate the effective potential between two large colloids immersed in a solution composed of depletant particles modelled as patchy colloids in which a hard-core repulsion is complemented by two or more short-ranged attractive 'sticky' spots [4]. At high cosolute densities, we find that the effective potentials, despite being purely attractive, display unusual peaks. We associate these oscillations with enhanced ordering of the co-solute, e.g. nematic for assembled linear chains, at characteristic distances, due to the confinement operated by the colloids [5]. We then show that such ordering is not exclusive of a pre-nematic behaviour but can manifest themselves whenever the depletant is modelled with directional interactions lying on a plane [6].

Finally we show that a variety of such effective potentials can be derived if binary mixtures of co-solute particles are taken into account [6]. In addition we show that the resulting effective potentials can be used to tune the lattice space of colloidal crystals paving the way for a new class of colloidal interactions occurring in crowded environments and biologically relevant systems [1, 2,].

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## State of the art of the interaction between cytolytic proteins and lipid-cholesterol bilayers

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*Bacillus thuringiensis* Cyt2Aa2 proteins show toxicity against insect larvae and some eukaryotic cells. Lipid-cholesterol bilayer models are a suitable tool to investigate their toxicity mechanism at molecular scale in the laboratory. In this talk, we will show how toxin concentration and observation time influence the lipid-protein interaction and the final nanostructure of the hybrid lipid-protein layer.

Quartz Crystal Microbalance with Dissipation (QCM-D) and Atomic Force Microscopy (AFM) studies reveal that the exposition of the lipid-cholesterol bilayer to 10 µg/mL protein concentration during two hours leads to the formation of aggregates (detergent-like mechanism). On the contrary, a rigid homogeneous lipid-protein layer is formed when the lipid system interacts with 100 µg/mL of toxin (pore-forming model mechanism) [1].

However, on one hand, QCM-D results indicates that at the lowest protein concentrations the hybrid system may not be at equilibrium. New AFM investigations confirm that those aggregates disappear forming a hybrid homogeneous layer similar to the case of the highest concentration (but more liquid-like) [2]. On the other hand, QCM-D results suggest that the addition of new proteins after seventy minutes leads to a new type of lipid-protein layer. Finally, AFM studies show that a second addition of protein to the lipid-cholesterol bilayer induces face separation in a time-frame of minutes.

Complementary studies concerning the interaction of lipid-cholesterol monolayers and the toxin has been carried out with Langmuir-Blodgett films. Preliminary results confirm the importance of the lipid/cholesterol ratio and the phospholipid chain length on the monolayer stability against the effect of cytolytic proteins (monolayer rupture).

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## Effects of ligand mobility on self-assembly of hairy disks

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We study the collective behavior of hairy disks in two-dimensional systems using molecular dynamics method. Nanoparticles are modeled as circular cores with three ligands. The ligands are linear oligomers. The chains are modelled as freely joined soft disks. All entities (either cores or chain segments) interact via Lennard-Jones (12-6) potential. The cut-off parameters are used to control interactions. The core-core and ligand-ligand interactions are assumed to be attractive, while core-ligand interactions are repulsive.

Similarly, as in previous paper [1] two models of hairy nanoparticles are considered. The first model involves particles with rigid geometry. In this case the grafting points are permanently fixed at vertices of an equilateral triangle inscribed into the core. According to the second model the grafted chains are mobile, they can slide over the core. Such a rearrangement of chains on cores are observed in experiments [2].

Our results indicate that the mobility of ligands affects considerably the self-assembly. We focus on the structure of the dense, liquid-like phase. The disks with rigid geometry form two different structures. The disks with attached trimers assembly into the hexagonal-like structure in which cores are located at vertices of hexagons and chains are accumulated inside these hexagons. The particles with longer ligands form the "spaghetti-like" structure built of strings of cores. On the contrary, the disks with mobile ligands always aggregate into the "wires" composing of double strings of cores with the ligands facing outwards. Such clusters, in turn, form the disordered structure or the highly ordered, lamellar phase. In all studied systems the mixed structure was found. We also show that ligand mobility plays a considerable role in the aggregation. The average cluster size is greater for nanoparticles with fixed ligands. Moreover, the distributions of cluster sizes calculated for fixed and mobile ligands are different.

The simulation results can provide guidance for preparation of new structures with important applications [3].

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## Vesicular structure formation of a triple-chain ion pair amphiphile

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Ion pair amphiphile, prepared from mixed cationic/anionic surfactants, can form vesicular structure (catanionic vesicle) in aqueous phase under certain conditions and can be applied in drug delivery [1]. In a previous study, it was demonstrated that stable catanionic vesicle with a positive charge character could be fabricated from a mixed double-chain ion pair amphiphile/double-chain cationic surfactant system with the addition of cholesterol [2]. However, a novel triple-chain ion pair amphiphile might exist in the mixed double-chain ion pair amphiphile/double-chain cationic surfactant system [3] and have the potential of forming vesicular structure in aqueous phase.

In this study, the vesicle formation behavior of a triple-chain ion pair amphiphile, prepared from a mixed double-chain cationic/single-chain anionic surfactant system, in aqueous phase was explored with the consideration of the added cholesterol effect. The triple-chain ion pair amphiphile, dihexadecyldimethylammonium-dodecylsulfate (DHDA-DS), was obtained from the aqueous mixture of dihexadecyldimethylammonium bromide (DHDAB) and sodium dodecylsulfate (SDS), and its composition was confirmed by the elemental analysis. It was then demonstrated that a dispersion of stable vesicle structures was able to be fabricated from DHDA-DS through a forced formation process. Moreover, the vesicular structures in the dispersion could maintain stable at high dilution ratios. The fluorescence polarization analysis implied that DHDA-DS molecules formed a rigid bilayer structure at room temperature, and the dynamic light scattering analysis suggested that the phase transition temperature of the vesicular bilayers was about 51°C. With the presence of cholesterol in the vesicular bilayer structure of DHDA-DS, it was found that stable vesicles could be fabricated. The effects of added cholesterol on the vesicular bilayer fluidity were then elucidated by fluorescence polarization and infrared spectroscopy analyses. The findings have implications for developing novel catanionic vesicles as drug delivery carriers.

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The motion of particles in a temperature gradient is known as thermophoresis [1]. We present thermophoretic measurements in aqueous suspensions of three different polystyrene (PS) particles of varying negative charge, size and surface coating. Our measurement technique is based on the observation of the colloidal steady state distribution using conventional Bright-field microscopy, which avoids undesirable effects such as laser-induced convection or local heating. We find that the colloids with the weakest zeta potential exhibit the strongest thermophoretic effect, suggesting that surface functionality leads to a more intricate dependence of the Soret coefficient on hydrodynamic boundary conditions than predicted by existing theories [2,3]. Furthermore, we propose a model to quantify the relaxation speed to steady state, based on the time evolution of the colloidal center of mass. Our observations are well described by this model and show that the relaxation speed tends to increase with the magnitude of the thermophoretic force.

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## Adsorption of soft particles at supported lipid bilayer

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Soft particles that feature a volume phase transition have widely applications in biomedicine such as drug delivery, biosensor and tissue engineering. Understanding how such a material interacts with lipid bilayer will potentially have a high impact on improving their drug delivery capability and reducing nanotoxicity [1]. Soft PNIPAM particles were found to densely pack in 2D hexagonal arrays at fluid supported lipid bilayer (SLB) rather than at solid SLB. The crystal packing at fluid SLB is reversible with a temperature cycle. Above the volume phase transition temperature ( $T_{VPT} = 32$  °C) of the PNIPAM microgels, the solid particles partially desorb and randomly distributed at fluid SLB. The softness and deformability of these types of particles play a major role in forming crystal. The observed self-assemblies, where the adsorption and position of the particles at supported lipid bilayer can be controlled “on demand”, opens new routes for the design of drug delivery system.

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## Colloidal crystal size evaluation: Scherrer vs. Laue

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Charged colloidal systems are well known model systems to study the phase behavior and crystallization kinetics of solids on a mesoscopic scale [1]. Their interaction closely resembles that of hard core Yukawa spheres used in computer simulations [2]. We are here interested in the interfacial free energy between the emerging crystal nuclei and the surrounding meta-stable shear-melt. According to classical nucleation theory, these should strongly influence the nucleation rate densities and – in combination with the meta-stability dependent crystal growth velocity determine the resulting crystallite size distribution [3]. Recently, we found that the interfacial free energy in such systems decreases with increasing polydispersity of the particles [4]. In the present paper, we therefore determine the interfacial free energies from measurements of the crystallite size distribution by static light scattering. The latter is typically evaluated from the width of Bragg reflections following Scherrer [5, 6]. We here test an alternative evaluation based on a procedure originally proposed by Laue [7]. The average crystallite sizes obtained from these methods differ systematically, but only by about 10%. This does not significantly influence the inferred interfacial free energies. We then compare our data on the reduced interfacial free energies extrapolated to zero meta-stability with the data sets available from literature. Furthermore, we discuss our findings with respect to the recent proposal of a decreasing interfacial free energy for increasing polydispersity. After a first evaluation the new data point taken on our low polydispersity sample contradicts the previous data. Possible origins of this deviation are discussed.

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## On the interaction of dipolar filaments

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Magnetic materials with elongated linear shapes can be found in many areas such as biology (magnetotactic bacteria [1]), medicine (drug delivery [2]) or nanotechnology (ultra-high density magnetic storage [3]). It is in this framework that the interaction of magnetic filaments such as needles and chains are investigated theoretically [4]. By revisiting the effective interaction of dipolar needles, we can better understand and characterize the interaction of magnetic chains. The most significant effect for the interaction of needles is the softening occurring at short separation characterized by an inverse power law  $R^{-1}$  of the inter-needle separation  $R$ . The origin of this softening is a long-range screening mediated by attractive pairs compensating the repulsion stemming from neighboring pairs. Dipolar chains exhibit a typical hardening at very short separation, in strong qualitative contrast with the needle behavior. This specificity is due to the discrete nature of the chains that enhances the repulsion near contact.

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## Heterogeneous Dynamics of Concentrated Silica-PNIPAm Core-Shell Systems

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Poly(N-isopropylacrylamide) (PNIPAm) cross-linked microgels show a coil-to-globule transition in water at a lower critical solution temperature (LCST) around 32°C, below which it swells by imbibing the solvent [1]. With this volume phase transition PNIPAm is applicable in both technical [2] as well as medical fields [3]. It furthermore became a frequently studied system in soft matter research as a model system to probe the specific phase behavior of soft colloids [4]. Via x-ray photon correlation spectroscopy (XPCS) [5] we investigate the change of structure and dynamics of highly concentrated PNIPAm core-shell microgels around the LCST.

Here we will present our work on particles with radii of 80-200 nm, whereby the PNIPAm shell thickness is varied on a silica core of constant size. We investigated the dynamics and interaction of the highly concentrated colloids as a function of temperature around the LCST as well as the modifications due to their swelling and deswelling behavior. Upon heating from room temperature to 40°C we found three dynamical regimes: First, the relaxation time decreases linearly while the shell shrinks. Second, around the LCST at 32°C the relaxation time decreases rapidly until it (third) jumps around 38°C more than three orders of magnitude. This effect was determined as a function of concentration between 6 and 30 wt% and is not present in dilute systems [6]. Furthermore, both the structural and the dynamical behavior were found to be reversible upon cooling down the system after heating.

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## Forces between similar and disimilar interfaces in solutions of the multivalent ions

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Forces between positively charged amidine latex (AL) and negatively charged sulfate latex (SL) particles were measured using colloidal probe force microscopy. [1, 2] Surface forces in all three possible combinations of particles, namely AL-AL, SL-SL (symmetric) and SL-AL (asymmetric), were examined in the presence of multivalent ions. At larger distances, the double layer forces can be quantitatively interpreted for all three combinations of particles using the Poisson-Boltzmann equation for asymmetric electrolytes containing multivalent ions provided that charge regulation of the surfaces is taken into account. The analysis of the double layer forces revealed that the multivalent counterions strongly adsorb to the charged interfaces which eventually leads to charge inversion. Counterion adsorption notably manipulates the surface regulation properties.

At distances less than few nanometers, there are omnipresent additional attractive forces which can not be described within classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO). These non-DLVO forces can be modeled with an exponential force profile. These forces are more long-ranged for the cases that multivalent ions act as counterions and the range of attraction can exceed 1 nm. The forces maximize at intermediate concentration of multivalent ions and vanish at very high ionic strength.

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## Thermo-optical trapping and manipulation of individual nanoparticles

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We present a single nano-object trapping and manipulation in an aqueous medium by optically induced temporally varying temperature gradients. By real-time object tracking and control of the heating spot position, we are able to precisely employ thermophoretic drift to oppose random diffusive motion. As a result, the nano-object is confined in a micrometer sized trap. Traps can be dynamically created and relocated which we demonstrate by a controlled independent manipulation of two nanoparticles.



## Eutectic Crystal Structures in Binary and Ternary Charged Colloids due to Depletion Attraction

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Colloidal crystals are ordered structures of submicron-sized uniform particles in two- or three-dimensions. Because their Bragg wavelengths can be identified in visible to near infrared regions, over the past few decades, colloidal crystals have been investigated as potential photonic materials. Recently, the fabrication of complex structures in multi-component colloids has attracted considerable attention. Here, we report the spontaneous formation of eutectic structures in binary and ternary aqueous colloidal dispersions[1]. These structures were formed because of interplay of crystallization of constituent components and accompanying fractionations in the multi-component colloids. The lattice planes of the resulting crystals were oriented parallel to the bottom plane of the container. The structures could be confirmed by direct observation with microscope and reflectance measurement. We obtained an observed binary phase diagram, defined by a mixing ratio and inverse area fraction of the particles, which was analogous to that for atomic and molecular eutectic systems.

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## pH reversible encapsulation of oppositely charged colloids mediated by polyelectrolytes

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We report the first example of reversible encapsulation of micron-sized particles by oppositely charged submicron smaller colloids. The reversibility of this encapsulation process is regulated by pH-responsive poly(acrylic acid) (PAA) polyelectrolytes present in solution. The competitive adsorption between the small colloids and the PAA on the surface of the large colloids plays a key role in the encapsulation behavior of the system. pH offers an experimental knob to tune the electrostatic interactions between the two oppositely charged particle species *via* regulation of the charge density of the PAA. This results in an increased surface coverage of the large colloids by the smaller colloids when decreasing pH. Furthermore, the PAA also acts as a steric barrier limiting the strength of the attractive forces between the oppositely charged particle species, thereby enabling detachment of the smaller colloids. Finally, based on the pH tunability of the encapsulation behavior and the ability of the small colloids to detach, reversible encapsulation is achieved by cycling pH in the presence of the PAA. The role of polyelectrolytes revealed in this work provides a new and facile strategy to control heteroaggregation behavior between oppositely charged colloids, paving the way to prepare sophisticated hierarchical assemblies. [1]

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## Pressure mediated phase transition in phoretic nematic colloids

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Colloidal microparticles dispersed in a liquid medium present a rich variety of interactions, even more when an external field is applied[1]. When the host is a nematic liquid crystal (NLC), inclusions can be driven by means of liquid crystal-enabled electrosmosis (LCEEO)[2]. This process is based on the unbalanced ionic flows at both sides of the inclusions coupled to the local orientational distortions of the nematic matrix. Peanut-shaped colloidal inclusions guarantee a dipolar component in the defect configuration of the local director field. The use of alternating current (AC) is of special interest in this case because ion migration is avoided, while enabling not only solid particle transport but water-based cargoes as well[3].

Experimentally, we prepared hybrid LC cells with plates coated with a transparent electrode. One plate was functionalized with a photosensitive self-assembled monolayer, which can turn the local director field from homeotropic to planar anchoring of the NLC under UV forcing. The reverse modulation is achieved with blue light. The counterplate was treated with a polyimide resin to obtain a strong homeotropic anchoring of the mesogen. Using an illumination with a Gaussian spot of light, this results in two main LC conformations and corresponding colloidal assemblies: aster (pure splay texture) or vortex (bend-splay texture, which induces a rotating mill).[4]

In this contribution, we address a point-focused colloidal phase transition between a solid-like and a liquid-like configuration, mediated by the LCEEO phenomena, and also the dependence of the steady-state distance between particles on the frequency of the electric field when self-assembled. Aster and rotating mill assemblies, where a centripetal force points towards the central defect point, features similar behaviour respect a frequency change. The theoretical model developed and further simulations performed are in completely qualitative agreement with the experimental results.

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## Synthesis of bi-functional Janus colloids

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Janus particles are colloidal analogues of molecular amphiphiles that can self-assemble into diverse structures. The chemical difference between the two patches of Janus colloids determines their configuration and stability. It is thus desirable to be able to prepare colloidal particles of which the two patches can be modified independently. By tuning the amphiphilicity, these colloidal molecules can then be used as colloidal surfactants in bulk or at liquid interfaces.

Here we report a versatile approach to prepare micrometer-sized Janus dumbbells that contain a brominated or chlorinated seed lobe, and a poly (3-(trimethoxysilyl) propylacrylate) (TMSPA) lobe. We show that each lobe of the Janus dumbbells can be modified independently. The brominated or chlorinated patches can be easily converted into other chemical groups, or grafted with polymers, while the TMSPA lobe can be further modified with silane coupling agents bearing different functional groups. In addition, we demonstrate that the size ratio of the two lobes can be adjusted by growing the TMSPA lobes to a desired size. Finally, this surfactant-free synthesis procedure makes the resulting particles ideal as colloidal surfactants.

## Microscopy of colloidal particles at an oil/water interface with an external electric field

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Colloids adsorbed at liquid/liquid- or liquid/gas-interfaces experience capillary interaction that cause the particles to attract or to repel one another [1]. This phenomenon comes from the deformation of the interface by the particles. The deformation of the liquid surface depends the shape of the particles and the wettability of the particles' surface. Other than capillary interaction, particles at the interface can also experience electrostatic interactions that are different from particles in the bulk. Here, we aim to study the colloidal interactions that take place when an external electric field is applied.

Particles positioned at the interface act as a dipole when an electric field is applied perpendicular to the interface; the particles will therefore repel each other. Another effect that can arise is that the electrified particle changes in height with respect to the interface, due the different dielectric constants of the particle and the two liquids. This affects the shape of the interface and thus the capillary interaction. This complex coupled interaction between electric repulsion and field dependent capillary interaction has been studied theoretically and numerically for spherical particles [2,3]. Experimental studies have been performed on uniformly shaped particles, larger than 1  $\mu\text{m}$  [4]. Since the shape and wettability will greatly influence the capillary interaction between the particles [5], tuning these parameters along with the electric field will allow us to form a rich variety of colloidal structures at the interface.

To study these interactions, we developed an electric cell that allows one to observe the top view of the interface, while the particles are subjected to a high external electric field. Important is that the interface is macroscopically as flat as possible, thus without capillary rise at the side walls. This is to reduce that the curvature has an effect on the particle distance. The height of the cell has to be as small as possible to facilitate the generation of high electric fields, but large enough to enable the tricky task of stacking two layer of liquids, with colloidal particles at the interface. The cell design and first microscopy results will be presented on this poster.

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## Static structure factor for a fluid with interaction of hard spheres plus two Yukawa tails

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We determine the static structure factor  $S(k)$  for a fluid of hard spheres with two Yukawa interactions through the application of the mean spherical approximation (MSA) to a multicomponent system composed of hard spheres plus double Yukawa interaction (HSDY). This  $S(k)$  depends on scaling parameters  $\Gamma_n$  that satisfy a system of nonlinear equations. We present explicit results for a mono-dispersed HSDY fluid and show that the hard-sphere contributions control main peak of the  $S(k)$ , while for wave vectors approaching zero, we predict a cluster peak which could be identified with that of recent experimental results [1]. We can use these results to calculate  $S(k)$  for a colloidal fluid and compare it with the experimental results in order to model their interaction under a very simple approximation [2].

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## The stability of high concentration whey protein systems and the influence of pH and salt.

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The stability of milk proteins over a range of solution conditions is an acute issue for processing in the dairy industry. High concentration protein solutions are desirable, but inherently unstable due to protein aggregation. The mechanisms leading to aggregation are complex, but include stresses imposed by heating and changes to pH and salt concentrations. Therefore, there is a need to understand the processes leading to aggregation for this protein system [1].

$\alpha$ -lactalbumin is a calcium binding whey protein and accounts for 28% of the protein present in milk. Upon heating above its melt transition temperature ( $T_m$ ), allowing unfolding to occur, it can refold when cooled. Depending on the solution conditions used, irreversible protein aggregation can occur after unfolding. Using Differential Scanning Calorimetry (DSC) [2] we show that  $T_m$  and the degree of reversibility of the unfolding process are altered by both pH and salt concentration. We focus on the role of calcium salts in modulating the solution and thermal stability of the protein.

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# Spatial confinement governs orientational order in one-patch particles

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A patchy colloidal particle is an ideal model anisotropic colloid due to its well-defined interaction anisotropy. Patchy particles exhibit novel positionally-ordered, i.e. crystalline, phases [1]. In addition, purely orientationally-ordered phases have been realized in closely packed spherical one-patch particles [2], which cannot be attained with shape anisotropy. Orientational order is expected to realise unique material properties compared with those by positional order, as known for magnetic or dielectric properties by the orientational order of dipoles in atomic / molecular condensed matter. However, the great variety of the phases in patchy particles often results in the degeneracy of the ground states, and a system easily falls in a metastable state or mosaic structure of the orders with similar energy.

In this contribution, we study the confinement effect on the orientational order in closely packed one-patch particles between flat substrates, both experimentally and with a numerical simulation [3]. In the experiment, the particles are monodisperse silica in diameter 1 – 2  $\mu\text{m}$ , with a deposited gold patch in 30-40 nm thick. The particles are dispersed in a 2,6-lutidine / water mixture and densely packed into quasi two-dimensional space by centrifugation in a wedge-shaped cell. We study orientational orders in tetragonal and hexagonal multilayers up to four particle layers formed by the layering transitions. The standard Monte-Carlo simulation was also performed, where completely spherical shape of a particle is assumed and inter-patch attraction is constant over the area of a patch.

The results of the experiment and simulation agree qualitatively, where a variety of ordered states appear dependent on patch size and confinement thickness: System geometry and boundary conditions select a commensurate state(s) from the (meta)stable options in the bulk system [2]. In addition, when all of the states in bulk are incommensurate, even a unique order appear. Our study shows a new route for realizing and controlling the mesoscopic order in patchy particles, and the system would possess unique functionality due to the purely rotational response of the constituent to external fields and stimuli.

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## Density dependence of orientational order in one-patch particles

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Closely packed spherical patchy particles exhibit a range of orientationally ordered equilibrium structures depending on patch size and particle arrangement due to the existence of a sticky inter-patch interaction and rotational degrees of freedom [1, 2]. These studies demonstrate that those purely orientational ordering can be an alternative to positional ordering for designing self-assembled mesostructures, and the ordered states may also exhibit unique material properties, as the orientational order of dipoles plays a significant part in determining the magnetic or dielectric properties of atomic / molecular condensed matter. In experimental patchy particle systems, however, a patchy particle is usually slightly aspherical e.g. due to the deposited patch on a spherical body, and particles must be slightly separated to avoid irreversible aggregation by van der Waals attraction [2]. The small shape anisotropy would thus lead to a coupling between translational and rotational motions, and packing density affects the orientational order, as generally known effect of compressive pressure on phase behavior.

We experimentally studied the packing density dependence of such ordering in particles with a thin deposited patch which imparts a shape anisotropy of a few percent in aspect ratio. These are confined between flat substrates with a chamber thickness of up to two particle layers. When the particles are tightly packed and almost in contact with each other, the anisotropic hard-body interaction dictates the orientational order and thus the order depends little on patch size, with rotational motion almost frozen. A small decrease in the density allows free rotational motion while translation is restricted to vibrational motion. This drastically changes the ordering which takes place, giving rise to a patch-size dependent equilibrium orientational order [2]. Furthermore, within this density regime, we found yet another density-dependent transition within the tetragonal bilayer. This transition is reproduced by numerical simulation assuming no shape anisotropy, indicating that translational entropy can play a significant role in determining the equilibrium orientational order, even in such a closely packed structure. Our study demonstrates the sensitivity of the ordering mechanism and resulting order on the packing density, where the effect of such a tiny shape anisotropy is clearly observable owing to the patch opacity. The dependence of cluster structure in particle dispersions on patch size, confinement thickness and packing density is also reported.

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## Adsorption and Crystallization of Charged Colloids on Polymer Modified Glass Substrates

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Charged colloidal particles dispersed in water self-assemble into crystal structures, when the electrostatic interaction between the particles is sufficiently strong. We have thus far investigated the adsorption of the colloidal particles on flat glass substrates in water. Because of strong van der Waals attraction between the colloidal particles and glass substrates, the particles are strongly adsorbed and fixed on the glasses.

In this study, we tuned the particle-substrate interactions by modifying the glass surfaces with hydrophilic polymers and controlled the particle adsorption. Adsorption behavior was examined at various polymer chain lengths, salt concentrations in water, and charge numbers of glass surfaces. We will also report 2D crystallization of the adsorbed particles on the substrates.

## Modulating protein-protein interactions in high concentration protein formulations.

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The stability of liquid protein formulations, such as immunoglobulin (IgG), is critical to the production, storage and efficacy of biopharmaceutical drugs. High concentration formulations with low viscosity properties are desirable to facilitate facile drug administration for patients [1]. Excipients are commonly added to protein formulations to improve the colloidal and structural stability of these products [2-3]. Given the different mechanisms by which protein self-association can proceed, appropriate selection of the correct formulation can be complex. The nature of the protein surface, pH, ionic strength, buffer type and the addition of excipients strongly influence the final stability of a given formulation [4-5]. Often, stability studies focus on low protein concentration formulations ( $\leq 10 \text{ mg ml}^{-1}$ ), however the behaviour of such dilute protein solutions may not adequately represent the high concentrations that are typical of biopharmaceutical formulations [6]. In this study the colloidal and structural stability of moderate to high concentrations of liquid protein formulations were evaluated using static and dynamic light scattering and differential scanning calorimetry to ascertain the best conditions to minimize protein self-assembly during production and storage.

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## Dynamics of Charged Colloids in Inhomogeneous Concentration Fields

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Recently there has been a lot of studies about the dynamics of colloids under nonequilibrium conditions. Here we propose a numerical model to study the dynamics of charged colloidal particles under inhomogeneous concentration field of a weak base.

We construct a model taking into account electrostatic adsorption of a weak base on the surface of colloidal particles and carry out numerical simulations using this model. We numerically solve the reaction-diffusion equation in 2D system placed between two reservoirs which have different base concentrations. The charged colloidal particles have the various charge number in the inhomogeneous concentration field of the weak base. To evaluate the force acting on the particle, we solved the Poisson equation numerically to obtain the electrostatic potential profile.

Our results show that a density gradient of colloidal particles are formed as a response to a weak base concentration field. Deep electrostatic potential in the vicinity of highly charged particles located in high base concentration field causes strong repulsive force to surrounding particles. At steady states, particles prefer low base concentration region because of strong repulsive force from particles placed in high concentration region. Thus, the particle density gradient is formed opposite to the base concentration gradient.

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Fractals are observed in many different systems, which exhibit self-similarity over a large range of time or space. Fractal properties have been studied in various realizations, however little is known about the impact of fractal confinement on the local structure and topological defects of ordered soft matter, such as liquid crystals. We studied three successive fractal iterations of Koch-shaped colloidal particles dispersed in nematic liquid crystal to characterize their impact on the surrounding nematic liquid crystal, by polarization optical microscopy and numerical modelling.

We use two-photon laser lithography to create Koch-shaped hollow colloidal prisms of three successive fractal iterations. We characterize the coupling with the surrounding nematic field by dispersing the Koch-shaped prisms in a low birefringent nematic mixture and observing the orientation and topological defects of the enclosing nematic field. We find an explicit geometry-induced generation of topological defect pairs, which follow an exponential-law dependency reaching few 100 already at fractal iteration four. Each pair is composed of a defect and its anti-defect, thus assuring the conservation of the total topological charge in agreement with Gauss-Bonnet theorem.

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## Optically Transparent Dense Colloidal Gels

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Usually it is difficult to image deep inside a dense colloidal gel purely because of the difference in refractive indices between the colloids and the fluid phase. These samples become opaque even at low colloidal volume fractions, preventing the study of structure of dense colloidal gels and transport through them. To solve this problem, we synthesize fluorinated latex (FL) colloidal particles [1] from heptafluorobutyl methacrylate which have a low refractive index ( $n = 1.37$ ) and thus can be index-matched in aqueous solutions. We subsequently functionalize them with short DNA sequences by first coating them with a dense brush-layer of polystyrene-*b*-poly(ethylene oxide)-azide (PS-PEO-N<sub>3</sub>) block-copolymers via a swelling-deswelling method [2] and then attaching the DNA to the azide groups on the PEO ends via a strain-promoted alkyne-azide click reaction. We study the structural differences of single gels made of only FL-particles and only PS-particles and composite gels made of percolating FL-gel coated with PS particles [3]. We also demonstrate the ability to track tracer particles inside an FL-gel using Dynamic Differential Microscopy (DDM) and thus study the diffusion of macro-molecules in dense gels [4].

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## Aggregation and phase transition of colloids induced by optical tweezers and thermophoresis

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Optical tweezers are an appropriate tool to manipulate colloidal systems. We present here a technique based on optical trapping and thermophoresis to create and manipulate large aggregates of colloidal particles.

The system is a mixture in organic solvents of refractive index- and density-matched PMMA colloids that do not interact directly with the laser of the optical tweezers, and titania particles that can be trapped. Trapped titania colloids are heated by the laser beam of the optical tweezers and create a very localized temperature gradient in the fluid. Surrounding PMMA colloids experience this gradient and are subject to thermophoresis that causes their aggregation around the titania particle. The strength and the range of the thermophoretic effect are sufficient to create aggregates of several thousands of particles in a few minutes.

With confocal imaging, we characterize the dynamics of the growth of such aggregates and show in particular that they can induce the crystallization of colloids around the titania particle. The advantage of this method compared to direct optical trapping [1] and direct heating of the fluid [2] is that spherically symmetric aggregates can be created in the bulk of a sample. We suggest that this system could be used to study the evaporation of a nuclei of a dense phase in a colloidal gas by turning off the laser.

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As is well-known, one-dimensional systems with interactions restricted to first nearest neighbors admit a full analytically exact statistical-mechanical solution. This is essentially due to the fact that the knowledge of the first nearest-neighbor probability distribution function,  $p_1(r)$ , is enough to determine the structural and thermodynamic properties of the system.

On the other hand, if the interaction between second nearest-neighbor particles is turned on, the analytically exact solution is lost. Not only the knowledge of  $p_1(r)$  is not sufficient anymore, but even its determination becomes a complex many-body problem. In this work we systematically explore different approximate solutions for one-dimensional second nearest-neighbor fluid models. We have applied those approximations to the square-well and the attractive two-step pair potentials and compared them with Monte Carlo simulations, finding an excellent agreement.



## Structural properties of the Jagla fluid

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The structural properties of the Jagla fluid are considered. The Jagla intermolecular pair potential is a spherically symmetric potential consisting of a short-range hard core, a repulsive linear shoulder, and a linear attractive well. It belongs to a family of so-called core-softened potentials and has been invoked to cope with thermodynamic anomalies such as reentrant melting and the density anomaly and in connection with liquid-liquid phase transitions in water and other substances. Moreover, the Jagla potential includes as interesting particular cases the ramp and the triangular-well potentials.

The underlying assumption of the present work is that it is possible to get an adequate representation of the Jagla fluid by using a potential with a hard core and an appropriate combination of square shoulders and square wells. The structural properties of such a model are in turn obtained from the application of the (semi-analytical) rational function approximation (RFA) method and, assuming that both potentials lead to the same cavity function, once the radial distribution function of the hard-core plus piecewise constant steps has been determined, the one of the Jagla fluid readily follows. The predictions obtained from this approach are compared against Monte Carlo simulations and numerical solutions of integral equations for the Jagla model.

## Anisotropic colloidal systems as models for island formation in monolayer growth

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The study of the controlled and efficient deposition of particles (atoms, molecules, nano-particles) on solid substrates has a wide range of applications in microelectronics, photonics, catalysis and in the production of special coatings and biological sensors, among others. In the last decades colloidal systems have been investigated as tunable and helpful models to describe different phenomena in condensed matter. In this work we present a colloidal model for studying some fundamental aspects of the early stages of epitaxial growth (submonolayer regime). Our model consists of a suspension of spherical colloids interacting through anisotropic pair potentials, which are in contact with a fix substrate. We performed Brownian dynamics simulations to investigate the aggregation kinetics of particles on the substrate in the early stages of the layer formation, in which nucleation and growth of islands are the dominant processes. Using several control parameters (i.e, anisotropy, intensity and range of the interaction, particle concentration in the suspension, substrate lattice constant, and strength of an external sedimentation field) we statistically describe the basic structural properties of the forming layer. In particular, we show the dependence on the different parameters of the island size distribution, the spacing between island (gap distributions), and the densities of monomers and islands as a function of time. The results obtained by numerical simulations are compared with a self-consistent analytical models reported in the literature [1, 2] and with those of Kinetic Monte Carlo simulations [3, 4].

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Calcium-silicate-hydrate (CSH) is formed from the hydration of  $C_3S$  and precipitates around clinker grains allowing them to bind together. The structural and kinetic features of the formation of the CSH amorphous phase have been recently studied by numerically simulating the precipitation process using a polydisperse colloidal model [1, 2, 3, 4]. Among the goals of nanotechnology research applied to construction materials is the search of nanocomposites that enhance the properties of cement, and the addition of superabsorbent polymers to enhance freeze-thaw resistance or thermoplastic polymers as additional binding agents are examples of such practices [5]. In this work, we study the effects that the addition of linear polymers has on the CSH precipitation. We employ MD simulations of the recently proposed colloidal system along with a coarse-grained model of the polymers in order to systematically analyze the effect of the latter on the properties of the previously studied precipitation model. We study the consequences of changing the interactions between the components of the system, the rigidity, length and concentration of the polymers, as well as, the precipitation rate.

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# Screening, hyperuniformity, and instability in the sedimentation of irregular objects

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We study the overdamped sedimentation of non-Brownian objects of irregular shape using fluctuating hydrodynamics. The anisotropic response of the objects to flow, caused by their tendency to align with gravity, directly suppresses concentration and velocity fluctuations. This allows the suspension to avoid the anomalous fluctuations predicted for suspensions of symmetric spheroids. The suppression of concentration fluctuations leads to a correlated, hyperuniform structure. For certain object shapes, the anisotropic response may act in the opposite direction, destabilizing uniform sedimentation.

## Microscopic engine powered by critical demixing

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During the last few decades much effort has gone into the miniaturization of machines down to the microscopic scale with robotic solutions indispensable in modern industrial processes and play a central role in many biological systems. There has been a quest in understanding the mechanism behind molecular motors and several approaches have been proposed to realize artificial engines capable of converting energy into mechanical work. These current micronsized engines depend on the transfer of angular momentum of light, are driven by external magnetic fields, due to chemical reactions or by the energy flow between two thermal reservoirs [1, 2, 3, 4]. Here we propose a new type of engine that is powered by the local, reversible demixing of a critical binary liquid. In particular, we show that an absorbing, optically trapped particle performs revolutions around the optical beam because of the emergence of diffusiophoresis and thereby produces work. This engines is adjustable by the optical power supplied, the temperature of the environment and the criticality of the system.

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# Equilibrium and dynamical density functional theory in the canonical ensemble

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Classical density functional theory is an indispensable theoretical tool in soft condensed matter physics. It has been successfully applied to a vast variety of systems ranging from the hard sphere fluid to e.g. complex liquid crystals. Density functional theory is usually formulated in the grand canonical ensemble, in which the chemical potential is fixed and the number of particles fluctuates. On the other hand, experiments and simulations are often performed in the canonical ensemble, conserving therefore the number of particles. In the thermodynamic limit both canonical and grand canonical ensembles are equivalent. However, the structuring and self-assembly of real systems can depend crucially on the precise number of particles in the system. In particular, small systems such as e.g. finite colloidal clusters, are better analyzed canonically.

Approximate methods to obtain canonical averages from a grand canonical functional include the addition of a term to suppress the fluctuations in the number of particles [1], and a series expansion of the canonical density distribution in powers of the inverse average number of particles [2].

Here, we present two general and formally exact methods [3, 4] to, given a grand canonical density functional, obtain

- i. The canonical density functional and the canonical density distributions.
- ii. The exact adiabatic dynamics of the system in which the fluctuations in the number of particles present in dynamic density functional theory are absent.

Our theories apply to finite systems in and out of equilibrium and can be used to help to develop approximate density functional theories and to accelerate the minimization of grand canonical density functionals for finite systems.

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Physics of self assembly of objects, such as polar and magnetic particles, is simultaneously of interest to many branches of science and technology. In biology, tubular and helical structures made of polar molecules are relevant self-assembled objects, for instance, found in bacterial flagella and microtubules. Other instances of such self-assembled tubular structures can be found in various materials with specific building units that can be: carbon atoms, coiled carbon nano-tubes, or amphiphilic molecules. Also, the fabrication of continuous magnetic nanotubes of different materials (organic and inorganic) has triggered a broad research field. Still creation of magnetic tubes remains challenging. On the other hand, features seen in continuous magnetic tubes are possible to obtain in colloidal systems and even macroscopic systems of discrete magnetic particles. The self-assembly of attractive dipolar particles will be addressed in the first part of the presentation. The relevance of stacking rings in 3D tubes [1] is demonstrated as a ground state of system for a small number of particles. It is further shown that tubes are actually subclass of densely packed helices [2]. The theoretical findings are easily reproduced experimentally with millimetric spherical magnets. In the second part, it will be shown that (macroscopic) granular systems as well as colloidal systems potential can be used to quantitatively mimic the phases occurring ferro- and even anti-ferromagnetic tubes [3]. We will further demonstrate how resonant motion can be excited in the system and that self-assembled tubes of magnetic particles may represent ideal model systems to analyze for example magnetic resonance and polarization wave propagation (theoretically, as well as, experimentally).

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## Interplay between self-assembly and condensation in models with asymmetric patches

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The strongly directional interactions present in many systems (like polar liquids, proteins, DNA stars) promote self assembly and play a crucial role in their thermodynamic properties. The simplest models for these systems are the so-called patchy particles, the surfaces of which are patterned so that they attract each other via discrete “sticky spots” of tuneable number, size, and strength. Using Wertheim’s theory, we go beyond the most studied cases of equal symmetric patches (i.e. a single energy scale or interaction interaction strength between patches), by considering asymmetric patches (i.e. multiple energy scales of interaction between the patches). We obtain all the possible types of condensation (and lack of it) in terms of the types of aggregates that can form, for a model with 3 patches and up to 3 energy scales [1]. We then develop a general analytical scheme for studying the nature of criticality in general patchy particle models, i.e. with any number of patches and energy scales of interaction. We show that in the cases where condensation may be absent, the density expansion of the pressure contains non-integer powers. The values of these powers are, on the one hand, determined by the characteristics of the most stable aggregates and by the degree of asymmetry of the model, and, on the other hand, determine the phase properties of the models.

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## Thermo-reversible colloidal gels from fluorinated particles

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We have designed and synthesized a new colloidal water-based system where the particles can be easily density and refractive index matched. Exploiting reversible addition chain transfer (RAFT) emulsion polymerization, we are able to produce fluorinated particles stabilized by neutral-PEG terminated Macro-CTAs (chain transfer agents), used as surfmers. The addition to the solvent of sodium polytungstate, an inorganic salt widely used as a heavy liquid for gravity separation, can simultaneously match optical index and density of the NPs. In addition, since these fluorinated colloids do not swell at all in aqueous solvents, their volume fraction can be accurately determined.

The key feature of this colloidal system is that, because of the strong dependence of the PEG-water affinity with temperature, the dispersion microstructure can be finely controlled by heating [1]. At room temperature, water is a good solvent for PEG chains, and the dispersion is stable. As temperature is increased, water becomes a progressively worse solvent for PEG and a temperature  $T_c$ , which can be easily tuned with the addition of a suitable electrolyte, there is a sharp transition from a stable solution to thermo-reversible gel.

Using Photo Correlation Imaging [2], Fluorescence Microscopy and Differential Dynamic Microscopy we have studied the kinetic arrest, restructuring under gravity and melting upon cooling of colloidal gels forming by spinodal decomposition. The results will be compared with theoretical predictions for short range potential systems.

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There has been strong experimental and theoretical interest in studying controllable mechanisms for the self-assembly of particles of different anisotropic shapes and with functionalized surfaces.

We report recent progress in calculating theoretically, using mean-field theory and the Derjaguin approximation, the effective interactions between colloidal particles in near-critical solvents. In the case of approaching the critical point of the solvent from the phase-separated region, we present critical scaling functions describing the formation of liquid bridges connecting two anisotropic, chemically homogeneous colloids and the interplay with critical adsorption [1].

The critical Casimir effect stands out as being particularly suitable for driving the self-assembly between functionalized colloids because it provides both attractive and repulsive interactions depending on the chemical surface properties, as well as a sensitive control of their strength via minute temperature changes [2, 3]. Building upon previous studies concerning the critical Casimir interaction of colloids with patterned substrates [4, 5], we have calculated theoretically the effective force and effective pair potential between two Janus cylinders as well as between two Janus spheres [6].

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## Dipolar colloids: From filaments to helices

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Dipolar particles can self-assemble into a plethora of structures depending on the confinement, presence of external field, number of particles, etc. For instance, the typical resulting elongated linear shapes (of, say, assembled magnetic nanocolloids) have considerable potential applications varying from biomedicine (e.g., drug delivery, hyperthermia treatment) to nanotechnology (e.g., ultra-high density storage).

In the first part of the talk, the interaction of dipolar filaments, such as chains and needles, under a strong magnetic field is discussed [1]. The separation distance regimes where chains behave whether or not like needles (with identical linear magnetization) are analyzed. It is shown in particular that at short chain-chain separation, there is a remarkable hardening upon approaching two chains in registry, which is in qualitative contrast with the needle case.

In a second part, dipolar helices made up of magnetic (or ferroelectric) beads will be addressed. As far as a single helix is concerned, we recently showed that the cohesive energy is a non-monotonic function of the pitch [2]. The more delicate situation, but also very intriguing, concerns the interaction between dipolar helices. First results in this field will be presented too.

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## How roughness affects the depletion mechanism

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It is well known since the seminal work by Asakura and Oosawa (AO) [1] that large colloidal particles suspended in a dilute polymer solution suffer an effective short-ranged attractive interaction arising from the depletion of solutes between the colloidal particles, provided they are sufficiently close to each other. In the analytically soluble AO model, the colloidal particles are modeled as hard objects of arbitrary shape and the depletion agent as an ideal gas, whose interaction with the colloids is of the excluded volume type.

A peculiar prediction of the AO model is that the strength of attraction increases with the size of the colloidal particles, at fixed solute volume fraction, implying that macroscopic objects should feel extremely large attractive forces at short distances. Surface roughness contrasts this paradoxical consequences by inhibiting the depletion mechanism.

During the last decade, the interest in this topic has been revived since the surface morphology of the colloid can be used to tune the effective interaction. Rough colloids with different shapes have been produced experimentally in order to investigate the change in the interaction: From particles decorated with spheres or lithographically shaped to lock and key colloids.

Theoretical studies of the effects of roughness on depletion have been recently performed by Monte Carlo simulations [2] coupled with liquid state theories [3], in the case of colloidal particles decorated with smaller spheres immersed in an ideal gas. However, analytical expressions able to capture the main effects of surface roughness on the shape of the depletion interaction are still missing.

We developed a simple model, in the framework of the AO theory, able to describe the effects of surface roughness for a significant range of parameters. The resulting explicit expressions are easily computed for a large interval of all the relevant parameters of the problem. Comparison with the available numerical simulations [2] shows an encouraging agreement and allows to predict the onset of colloidal aggregation in dilute suspensions of rough particles.

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# Direct Measurement of Thermodynamic Properties of Dense 2D Colloidal Fluids using a Repulsive Optical Landscape

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Thermodynamic quantities of colloidal systems can be measured by tracking particles using optical microscopy and analyzing their coordinates using methods based on test-particle insertion and statistical geometry [1, 2, 3]. In spite of this, direct measurement of thermodynamic properties, in particular the chemical potential, remains a fundamental challenge at high densities where such methods break down [4].

A modification of the insertion method for inhomogeneous fluids [5] has been shown in simulation [6] to allow access to the chemical potential by perturbing a small region of the system with a repulsive external potential. We implement this method experimentally using a repulsive optical landscape, which produces a small low-density region in a high-density colloidal monolayer. At equilibrium, the chemical potential is easily measured in this region and, by definition, is identical to that in the bulk system. The method also admits measurement of the bulk pressure through integration of the density profile, thus allowing access to the free-energy density of the system. We confirm the validity of our method by comparing results obtained using an experimental hard-disk system [7] with Scaled Particle Theory [8]. The ability to measure key thermodynamic properties of dense systems opens the possibility of a full experimental study into the thermodynamics of two-dimensional fluids.

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## Dynamics of polydisperse colloidal systems: a mean-field lattice-gas theory

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We study phase separation kinetics in polydisperse systems via a new dynamical mean-field theory based on the Polydisperse Lattice-Gas model. The model gives a simplified description of colloidal suspensions, combining a hard-core repulsion with polydispersity in the strength of the attraction between neighbouring particles. Our mean-field equations describe the local concentration evolution for each of an arbitrary number of species, and for an arbitrary overall composition of the system. We focus on the predictions for the dynamics of colloidal gas-liquid phase separation after a quench into the coexistence region. We determine the relevant spinodal curves and critical points analytically, with the former depending only on three moments of the overall composition. The results for the early-time spinodal dynamics show qualitative changes as one crosses a "quenched" spinodal that excludes fractionation, allowing only density fluctuations at fixed composition. This effect occurs for dense systems, in agreement with a conjecture by Warren that at high density fractionation is generically slow because it requires inter-diffusion of particles. We verify this conclusion by showing that the observed qualitative changes disappear when direct particle-particle swaps are allowed in the dynamics. Finally we study the rich behaviour beyond the spinodal regime, where the evaporation of gas bubbles with strongly fractionated interfaces causes long-lived composition heterogeneities in the liquid phase; we introduce a density histogram method that allows such effects to be easily visualized for an arbitrary number of particle species.

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The dynamics of colloidal suspensions undergoing Brownian motion can be conveniently studied in real space using confocal microscopy. A key observable is the van Hove function  $G(r, t)$  which describes the relaxation of spatial correlations upon releasing a tagged particle. Of particular interest in colloidal physics are colloid-polymer mixtures, where the addition of polymers to the colloidal suspension gives rise to colloid-colloid attraction which is of entropic origin. In this contribution, we present results for  $G(r, t)$  in colloid-polymer mixtures obtained both from dynamical Monte-Carlo simulations and using classical dynamical density functional theory. Our theory employs the accurate fundamental measure free energy for the colloid-polymer mixture in the Asakura-Oosawa model [1], which we supplement with a suitable removal of self-interactions and a particle mobility depending on the local density distribution [2, 3, 4].

We obtain quantitative agreement between theory and simulations over a wide range of packing fractions. When the polymers move slowly relative to the colloids, we see a central peak in the distinct part of  $G(r, t)$ , similar to experimental findings in colloidal systems undergoing gelation [5]. Moreover, we observe that for slow polymers at constant reservoir packing fraction the colloidal mobility displays a maximum at an intermediate colloid packing fraction. This interesting non-monotonic behavior can be described by a simple semi-empirical formula.

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## Motion in diffusivity landscapes: Towards analytic correlation functions

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Anisotropic and anomalous diffusion in heterogeneous environments – governed by a landscape of energy and diffusivities – is a relevant and frequently studied phenomenon in experiment, simulation and theory. A paradigmatic example is water diffusion through hydration shells around biomacromolecules or membranes. Analytical fit functions for complex systems such as these are rare, although they would be interesting to connect conceptual ideas to experimental results.

We report on an approach to recover effects of geometry and position-dependent diffusivity by approximate solutions well-suited for data fitting [1]. In particular, we map the motion through a complex landscape on the stochastic switching in a network of dynamical states with approximated internal dynamics. First, we derive an analytical function for an isotropic motion switching in time between different diffusive states, which has been successfully used to describe the hierarchical subnanosecond dynamics of proteins [2]. Second, we extend the approach towards anisotropic systems such as layer structures, aiming for e.g. a description of anisotropic water diffusion around membranes [3]. Finally, we discuss the challenges, limitations and potentials of the outlined method for data analysis integrating experimental and theoretical knowledge.

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## Chiral Colloids from Isotropic Spheres

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Self-assembly of complex structures is usually assumed to require complex building blocks. For example, colloidal helical structures as models for the DNA helix have been assembled from complex anisotropic magnetic colloids [1] and amphiphilic Janus spheres [2]. However, more than a decade ago it was predicted that isotropic spheres can form helical structures upon cylindrical confinement due to simple geometric restrictions [3].

This prediction put us on the track of a new method for creating helical structures from micrometre-sized colloidal spheres. Mixtures of  $\beta$ -cyclodextrin ( $\beta$ -CD) and sodium dodecyl sulphate (SDS) form complexes in a 2:1 molar ratio at elevated temperatures. Upon cooling to room temperature these SDS@ $\beta$ -CD complexes self-assemble into hollow microtubes. By adding colloidal particles into the mix colloid-in-tube assemblies are obtained. Depending on the size ratio of the colloid-to-tube diameters chiral structures, including helical sphere chains, are formed [4].

In order to fix these chiral assemblies inside the microtubes to obtain stable chiral colloids even when the confinement is removed, photo-responsive colloids were synthesized. These colloids were subsequently crosslinked upon irradiation with UV-light as a result of the coumarin molecules incorporated on the particles' surface. Eventually, a library of ordered structures, such as linear chiral assemblies, zigzag and zipper configurations of isotropic colloidal spheres, has become available. We have started to explore our chiral colloidal chains for model studies of colloidal liquid crystal phases.

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## Iterative Reconstruction of Memory Kernels

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In recent years it has become increasingly popular to construct coarse-grained models with Non-Markovian dynamics in order to account for an incomplete separation of time scales. One challenge of a systematic coarse-graining procedure is the extraction of the dynamical properties, namely the memory kernel, from all-atom simulations. In this talk we will present the iterative memory reconstruction (IMR) [1], which is the first iterative method suggested in the field of Non-Markovian modeling. This new extraction technique shows various similarities to the reconstruction of static potentials *via* inverse Monte Carlo (IMC) [2] or iterative Boltzmann inversion (IBI) [3]. The big advantage compared to previously proposed techniques (e.g. [4, 5]) is the efficient reconstruction of coarse-grained models that have precisely the same dynamical properties as the original fine-grained systems.

We demonstrate the performance of the above described methods at the example of the anomalous diffusion of a single colloid. For this system we are able to reconstruct realistic coarse-grained models for timesteps about 200 times larger than the original molecular dynamics simulations.

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Confinement of mixtures of colloidal particles in evaporating emulsion droplets is an experimental technique to induce self-assembly of uniform superlattices. The resulting highly structured and symmetric colloidal nanocrystals could be used as building blocks in the design of novel functional materials. We explore the extension of this method to binary colloidal mixtures of variables sizes and materials. The structure diagram for binary clusters of Lennard-Jones particles is analyzed by means of a global optimization approach for a large range of cluster sizes, compositions, and interaction energies and present a publicly accessible database [1]. We determine the factors that influence the formation of clusters with specific properties and find a variety of structures such as core-shell clusters, Janus clusters, and clusters in which the minority species is located at the vertices of icosahedra. We test the equilibrium phase behavior of interesting structures for possible desired behaviour.

We also study the influence of the assembly environment on the attainable structures by changing the pressure inside confinement and propose the associated formation mechanism. Moderate pressure differences on the order of 100 kPa change the particles' self-assembly behavior [2]. Crystalline superlattices, Janus particles, and core-shell particle arrangements form in the same dispersions when changing the working pressure or the surfactant that sets the Laplace pressure inside the droplets. Molecular dynamics simulations confirm that pressure-dependent interparticle potentials affect the self-assembly route of the confined particles. Optical spectrometry, small-angle X-ray scattering and electron microscopy are used to compare experiments and simulations and confirm that the onset of self-assembly depends on particle size and pressure. The overall formation mechanism reminds of the demixing of binary alloys with different phase diagrams.

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Hydrodynamic interaction is a common mechanism by which various biological systems coordinate, including motile cilia [1]. Cilia are hair-like growths off a cell, the structure of which is highly conserved across species. The coordination of motile cilia is responsible for symmetry breaking during foetal development, as well as fluid transport in the brain and lungs [1, 2]. Synchronisation is a well known phenomenon in many biological systems. Classic examples include firefly flashing and Mexican waves, where the oscillator is a whole being, as well as dynamics of organs like the brain, heart, and lungs, where the oscillator is smaller component [3].

The chimera state is a combination of synchronised and incoherent subsets in a population of identical oscillators [4]. It is usually recognised by a subgroup developing disparate frequencies and losing synchrony. Originally thought a mathematical curiosity, chimera states have now been linked to heart complications, epilepsy, and uni-hemispheric sleep. They have been observed experimentally in optical and mechanical oscillators arrays, among many others.

Here the focus is on chimeras in arrays of rowers. Rowers are a simple model to study coordination of motile cilia that uses driven colloids [1]. Their interaction is based on hydrodynamics at low Reynolds' number, and has not previously been related to these states. We find that within the appropriate parameter range, simulated rower arrays will develop into chimera states.

The simulations use Brownian Dynamics and an Oseen tensor interaction [5]. The resulting collective states can be considered in two complementary contexts. The first is the system's eigenstate solutions, which are derived from the fundamental interaction between rowers. This approach has previously been applied to sets of rowers [6]. Alternatively the system can be linked to chimera states of Kuramoto-style oscillators. In this case the focus is instead on the mean interaction. We find the contrast between the approaches provides new insight into the collective dynamics and states in these colloidal arrays.

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## Free Energy Calculation of Colloidal Crystals. Application to Low Temperature Phases of the Lennard-Jones System

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The knowledge of the free energy is fundamental to determine the relative stability of different colloidal crystal phases in thermodynamic equilibrium. A very well-known method to compute free energies of crystals is the Einstein method of Frenkel and Ladd[1], where a thermodynamic integration connects the modelled system to an Einstein crystal, whose free energy can be calculated explicitly. The method is simple and elegant, but it requires very long simulations in cases where the free energies of two phases are very close.

In this contribution, we investigate a general method to calculate free energy of crystals by considering the harmonic approximation and quasistatically switching the anharmonic contribution [2]. The advantage of this method is that the harmonic approximation provides an already very accurate estimate of the free energy, and therefore the anharmonic term is numerically very small and can be determined to high accuracy. We further show that the anharmonic contribution to the free energy satisfies a number of exact inequalities that place constraints on its magnitude and allows approximate but fast and accurate estimates. We use the method to calculate the low temperature phase diagram for Lennard-Jones particles. We demonstrate that hcp is the equilibrium phase at low temperature and pressure and obtain the coexistence curve with the fcc phase, which exhibits reentrant behavior.

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Single-file diffusion is a ubiquitous physical process exploited by living and synthetic systems to exchange molecules with their environment.[1, 2] It is paramount to quantify the escape time needed for single files of particles to exit from constraining synthetic channels and biological pores. This quantity depends on complex cooperative effects, whose predominance can only be established through a strict comparison between theory and experiments. By using colloidal particles, optical manipulation, microfluidics, digital microscopy, and theoretical analysis we uncover the self-similar character of the escape process and provide closed-formula evaluations of the escape time. We find that the escape time scales inversely with the diffusion coefficient of the last particle to leave the channel. Importantly, we find that at the investigated microscale, bias forces as tiny as  $10^{-15}$  N determine the magnitude of the escape time by drastically reducing interparticle collisions. Our findings provide crucial guidelines to optimize the design of micro- and nanodevices for a variety of applications including drug delivery, particle filtering, and transport in geometrical constrictions.[3]

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## Defects in simple cubic crystals: Revealing the vacancy-analogue of the crowdion interstitial

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At finite temperatures, all equilibrium solid phases possess point defects, such as vacancies and interstitials. These defects arise as the free energy of the solid phase is always minimized by a small but nonzero fraction of such defects. In most systems, such point defects are fairly well localized to a specific lattice point. However, in some intriguing cases, point defects take on forms that are extended in space, such as the crowdion interstitial, as proposed by Paneth in the 1950s.

Here, we examine a novel, vacancy-analogue of the crowdion for a wide range of systems that form simple cubic crystals, including hard cubes, hard “tilted” cubes, and isotropic, repulsive spheres. Using computer simulations, we show that inside these simple cubic crystals, high concentrations of stable, extended vacancies defects manifest in the form of a row of  $N$  particles being spread over  $N + 1$  lattice sites. We track the positions of these vacancies and study their structure, dynamics and interactions. Similar to the interstitial-case, the strain-field of these extended vacancies follows the soliton solution of the Sine-Gordon equation. Additionally, we show that the diffusion of these vacancies is almost one dimensional at short time scales but for longer time scales the diffusion becomes isotropic.

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Recent progress in global-balance Monte Carlo algorithms has allowed to confirm the essentials of the Halperin-Nelson-Young theory (KTHNY) for the 2D Melting problem with short-range interactions [1]. A key challenge in these simulations are large correlation lengths which could be overcome by a new class of global-balance, rejection-free Monte Carlo algorithms, following the ‘Event-chain’ paradigm [2].

In this talk, I will show that Event-chain Monte Carlo algorithms can be extended to include long-range forces (including periodic images) rigorously, without truncation the interaction potential. The new algorithm improves on the scaling of Ewald summation [3], which enables significantly increased particle numbers in systems with charged or polar interactions.

As an initial application, I will present results on the 2D melting problem in the long-range limit, and complete the phase diagram of inverted power-law potentials, relevant for charged colloids, plasma crystals, and other systems.

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# From a driven passive to an active colloid in spatially periodic potentials

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Passive colloids driven above spatially periodic potentials exhibit nontrivial transport and can lead to such effects as depinning [1, 2], chain assembly [3], dynamic mode locking [4, 5], front propagation [6]. Simple periodic landscapes can be realized via arrays of optical traps [2, 4, 5] or by using stripe-patterned magnetic substrates [1, 3, 6]. These experimental systems can be mapped onto a class of simple analytically tractable models. We start from a brief observation of the main features of passive colloids and extend our analysis to the case of an active chemically activated colloidal particle. The latter is suspended under gravity and self-propels above a two-dimensional periodic layer build of closely packed particles whose size is comparable to that of the active particle.

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## Chains and Rings in Dipolar Fluids

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We investigate the self-assembly of magnetic nanocolloids by using a dipolar hard sphere (DHS) model. A DHS consists of a point dipole embedded in the center of a hard sphere, generating long-range anisotropic interactions. At low temperature DHS particles self-assemble into complex structures, with primary structures being rings and chains. Understanding the structures that emerge in the system is fundamental for designing new magnetic fluid-based devices for technological and medical applications.

We focus on computing the exact values of partition functions for DHS chains and rings consisting of an arbitrary number of particles. For that, firstly, we perform grand canonical Monte Carlo single cluster simulations. We introduce specialized Monte Carlo biased moves, which favor the breaking and reforming of bonds. Knowledge of the cluster partitions functions allows us to compute the free energy of systems at low-to-intermediate densities, where the clusters can be considered as non-interacting. Secondly, we compare previous analytical expressions [1] against the simulation data and improve them accordingly. In our new theoretical approach we separate the energetic and vibrational contributions of both the chain and ring free energies. Moreover, we introduce a re-scaling of the temperature to take into account the dipolar interactions between non-nearest neighbours along the cluster backbone. [2]

In this way, for the first time we can not only analyse the free energy of DHS chains and rings, but also shed light on the possibility of a hotly debated topological phase transition in this system. Our results will also allow us to describe the next level of hierarchical self-assembly in magnetic nanocolloids namely, the aggregation of branched clusters into complex networks.

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## Glassy orientational dynamics in plastic crystals of aspheric colloids

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Aspheric molecular or colloidal systems, with only a slight degree of anisotropy, often assemble into plastic crystals [1]. While plastic crystals exhibit the full positional order of a crystal, they can freely rotate around their center of mass, rendering them orientationally disordered. It is exactly this high orientational diffusivity which grants those materials high plasticity, making them good candidates for solid state electrolytes in fuel cells, batteries and solar cells [2]. In the colloidal realm, plastic crystals are often realized by sub-micron sized, polyhedral-shaped PMMA/polystyrene particles or nanocrystals.

In this work [3], we study the self-assembly process of truncated-hexbipyramid-shaped effectively hard Bi-nanocrystals in experiment and simulation and present evidence of glassy orientational dynamics in the plastic phase of this system.

Experimentally, we assembled the Bi-nanocrystal super-structure through diffusion of a non-solvent into colloidal nanocrystal suspension and studied the crystallisation process with small angle x-ray scattering (SAXS) at the synchrotron ELLETRA. To model the self assembly process in simulation, we used NPT Monte-Carlo.

At intermediate packing fractions, in experiment as well as in simulation, we find the system to assemble into a plastic-fcc crystal, as expected. However, it turns out that this so-called plastic crystal is not completely orientationally isotropic: Instead, six distinct orientations are taken on more frequently and, with increasing packing fraction, most particles assume one of these six global orientations. Upon increasing the pressure further, we find that, instead of transitioning into the more stable, parallelly aligned crystal, the system exhibits glassy behaviour. Reorientations remain possible, but occur in large orientational jumps, leading into one of the six global orientations. We compare this behaviour to the freezing of the six color Potts model where, after a very long time, the system becomes parallelly aligned.

We argue that glassy orientational dynamics upon freezing may not be unique to truncated hexbipyramids, but it might be a general feature of polyhedral plastic crystals. Hence, we hope that this work will inspire more research on the general properties of plastic-crystal to crystal transitions.

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# Dynamic Pair Correlations and Superadiabatic Forces in a Dense Brownian Liquid

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We present two-body correlation functions, i.e. the two-body density, the current-density correlator or van Hove current, and the current-current correlator in Brownian dynamics computer simulations of a dense Lennard-Jones bulk liquid [1]. The dynamic decay of the correlation shells of the two-body density is shown in detail. Inner correlation shells decay faster than outer correlation shells, whereas outer correlation shells remain stable for increasing times. Within a dynamic test particle picture the mechanism is assumed to be triggered by the dislocation of the self particle, which releases the confinement of the surrounding correlation shells. We present a division of the van Hove current into an adiabatic and a superadiabatic contribution. The magnitude of the adiabatic van Hove current is found to exceed that of the total van Hove current, which is consistent with dynamic density functional theory overestimating the speed of the dynamics. The direction of the superadiabatic van Hove current opposes that of the total van Hove current. The current-current correlator reveals detailed insight in the collisions of the particles. One finds a large static nearest neighbor peak, which results from colliding particles and different dynamic peaks, that are attributed to consecutive collisions.

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## Phase transitions on the surface of a sphere

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The phase transitions of systems of attractive colloids confined to the surface of a sphere are strongly influenced by the curvature of the surface. These influences include the frustration of crystal structures and the modification of the perimeter-area relationship of isotropic clusters of particles [1, 2]. In addition, the surface of a sphere is limited in extent, introducing finite size effects to the behaviour of systems confined to it. Moreover, these two influences cannot be considered in isolation as the curvature and area of a sphere are not independent.

Here, the nucleation and growth of a two dimensional liquid confined to a sphere is investigated by Monte Carlo simulation. The model system considered consists of colloidal particles interacting isotropically *via* the Lennard-Jones potential [3], and we measure the gas-liquid coexistence curve as well as the free energy profile for liquid nucleation from the gas phase. The influence of the curvature dependent nuclear geometry and finite surface size are clearly observed. Further we demonstrate that it is possible to construct modifications to classical nucleation theory (CNT) which capture the finite size of the system and the curvature dependent geometry of a cluster [2, 4].

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## Crystallization of star polymer under shear flow

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Controlling crystallization in soft colloidal systems represents a fundamental challenge for material design. Among different approaches for enhancing the crystal phase, there are evidences that the application of a shear flow may favour the formation of crystals [1,2], thus representing a new method to verify the existence of crystal phases predicted in several soft colloidal systems. In our work we numerically investigate the crystallization of star polymers induced by the presence of a shear flow. Star polymers, i.e. polymer chains anchored to a common centre, represent a favourite model system in soft matter being characterised by a rich phase diagram, encompassing multiple crystal phases. We simulate star-polymers using two Molecular Dynamics approaches: the first is based on SLLOD equations with Gaussian thermostat (MD-GAUSSIAN) and the second uses Dissipative Particle Dynamics thermostat (MD-DPD). The latter has the advantage to implicitly include the hydrodynamic effects of the solvent, which is neglected in the former approach. Our simulations show that a transition from fluid to solid occurs in both types of simulations but the crystals found are of different types, being bcc-like in MD-GAUSSIAN simulations and fcc-like in MD-DPD. Most interestingly, we find that in MD-DPD a two-step crystallization takes place from fluid to bcc and then to fcc, showing the occurrence of a crystal-crystal transition in simulations. This is in agreement with recent experimental results obtained with oscillatory shear flow, thus highlighting the importance of hydrodynamics in the crystallisation process under shear flow. Finally, we discuss what happens during the crystal-crystal transition by comparing our case with the recent work of Peng. Y et al [3] on 2D crystallisation of microgel particles.

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In 1930s, Gamow developed the liquid-drop model of the nucleus, transplanting macroscopic notions of pressure and surface tension to subatomic scale. We use a related approach to construct a coarse-grained model of soft polymeric nanoparticles, which allows us to evaluate their deformation energy when densely packed. By comparing the energies of model particles arranged in different crystal lattices, we compute their rich phase diagram, which contains many experimentally observed phases. The model offers a readily visualizable interpretation of micromechanics of soft nanoparticles, which can also be used to study rheology, dynamics, and glassy behavior of their dense suspensions.

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## Phase diagram of soft nanoparticles at interface

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We theoretically study the structure of a monolayer of soft nanocolloidal particles trapped at a fluid-fluid interface [1]. We use a coarse-grained representation where the particles are modeled as liquid drops characterized by a given reference volume and compressibility as well as two drop-fluid surface tension and one drop-drop interfacial tension [2]. We compute the free energy of the monolayer for several trial 2D lattices, and we construct the equilibrium phase diagram and the pressure-area isotherms of this quasi-2D system. The results are compared to a recent experimental study of core-shell microgel particles [3].

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## Elasticity of soft nanocolloidal crystals

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Using the liquid-drop model as a coarse-grained description of nanocolloidal particles such as star polymers and dendrimers [1, 2], we theoretically analyze elastic deformation of crystals formed by these particles. We focus on the face-centred cubic lattice stable immediately beyond the fluid-solid transition where the drop-drop interaction is pairwise additive and a linear function of indentation [2]. We compute the elastic free energy for the simple- and pure-shear deformation and we calculate the elastic moduli as a functions of model parameters as well as density. The results are compared to existing direct and indirect experimental reports of the moduli.

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# A model colloidal microphase former with anisotropic competing interactions

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Using classical density functional theory (DFT), we investigate systems exhibiting pair-interactions where a short-range anisotropic attractive force competes with a long-range spherically symmetric repulsive force. The attractive part of the interaction is modelled within Wertheim's first-order perturbation theory for patchy particles [1, 2], and the repulsive part is assumed to be a Yukawa potential which is taken into account via a random phase approximation (RPA). From previous studies of colloidal fluids with purely spherically symmetric competing interactions, it is well known that such system exhibit clustering and stable periodic microphase separation (inhomogeneous bulk phases) provided that the repulsion is weak compared to the attraction [3, 4, 5].

Employing the present model system with anisotropic competing interactions, we find a rich phase behavior including reentrant microphase separation and liquid-gas binodals. In particular, the model predicts inhomogeneous bulk phases at extremely low packing fractions, which is not observed in systems with isotropic competing interactions.

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We present an analysis of the condensation of counter-ions around a charged disk. The model under consideration is a two-dimensional (2D) system formed by an impenetrable disk of charge  $Q_1$  surrounded by ions of charge  $q$  dispersed freely in a larger disk with external charged boundary  $Q_2$ , at thermal equilibrium at a temperature  $T$ . In mean field, it is known that a disk with a dimensionless charge  $\xi = qQ_1/(2k_B T) < 1$  is unable to bind counter-ions. When the charge is above unity ( $\xi > 1$ ), it attracts an ion cloud in such a way that it neutralizes partially the disk so that the effective dimensionless charge of the disk and the cloud is unity. We explore the faith of this counter-ion condensation beyond the mean field regime for large values of the Coulomb coupling. In particular, for some special values of the coupling, exact analytical results can be obtained for the system, which give an interesting insight on the condensation phenomenon. These exact results can be obtained by recognizing that the Boltzmann factor of the system can be expressed in terms of a Jack polynomial, and expanding it in a monomial basis [1].

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## A model of self-electrophoresis of isotropic colloidal particles with chemical reactions

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We propose a dynamical model of self-electrophoresis of isotropic colloidal particles with chemical reactions. In this model, the colloidal (solid) particles are immersed in a weak electrolyte solution. On each particle surface, a certain amount of ionizable groups are distributed uniformly, and their dissociation gives rise to a charged surface. This charging process occurs as a result of surface chemical reaction with the weak electrolyte.

We describe the above system as a reaction–diffusion system including particles on which the chemical reaction takes place. The particles are not fixed but can move as a result of dissipative processes in the interfacial region between the solid particle and surrounding fluid. We assume the linear relationship between the slip velocity which causes the particle motion and the force acting on the surrounding fluid [1].

We carried out numerical simulations based on the above model. In the numerical calculations a particle was treated as a field with the smoothed profile which is similar to that introduced in references [2, 3]. It was also assumed that the electrolyte (base), counter-, and co-ions can diffuse but the ionizable and ionized groups are attached on the surface of particles and cannot diffuse.

Our numerical simulations of one-particle system with a homogeneous initial condition show that the stationary state becomes unstable for some parameters and the particle starts to move. This self-propulsion of the particle occurs when the charge distribution on the particle breaks the spatial symmetry and the particle moves in a certain direction, simultaneously.

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# Crystallization of ultra-soft particles on periodic substrates: A systematic density functional theory study of surface-induced phase transitions

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We investigate a system of soft particles with varying steepness of the interaction potential in a 2D system within the framework of density functional theory (DFT) and dynamical density functional theory (DDFT). Depending on system parameters, we find a homogeneous fluid phase or crystallization. In contrast to previous studies on 3D systems [1,2], here we focus on a 2D system in order to gain access to the behaviour in flat geometries or on surfaces, which was started in Ref. [3,4]. Furthermore, we systematically study the influence of the steepness of the interaction potential. We compare calculations based on free minimization within DFT with estimates based on linear stability analysis of the fluid state, which yields good agreements for all steepness values.

We then turn our attention to the self-assembly of colloids on prestructured periodic substrates, which can, if suitably designed, be used as templates for multilayer crystal growth and furthermore allow to create novel 2D morphologies. In particular, we address the key issue of how to achieve well controlled manufacturing: "What is the optimal design of the substrate to enhance regular, defect-less nano patterns?"

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We investigate the probabilistic treatment of classical overdamped noisy systems with time-delayed forces (that depend on the system state at a discrete earlier time) in the steady state. Due to the non-Markovianity, there is no standard Fokker-Planck equation (FPE) that corresponds to the delayed Langevin equation (LE). On the contrary, the Fokker-Planck approach yields an infinite hierarchy of coupled differential equations [1].

We present a closed approximate FPE for the one-time probability density of such non-Markovian systems, obtained by a force linearization in all members of the infinite hierarchy, starting from the second. The approach applies to a wide class of nonlinear deterministic forces, and yields much better results compared to an earlier LE-based approach by Guillouzac *et al.* [2]. It further does not rely on any other quantities (for which additional approximations can be inevitable), in contrast to the perturbation-theoretical approach introduced by Frank [3]. Applying the approaches to two generic exemplary systems, we demonstrate that our ansatz provides an improved approximation of the one-time probability density. We furthermore discuss the possibility of accessing transport-related quantities, such as escape times.

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## Comparison of different methods for calculating effective interactions and pressure in charge-stabilized dispersions

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Charge-stabilized suspensions have interesting static and dynamic features, reflected in properties such as the suspension osmotic pressure, generalized sedimentation coefficient and viscosity. These properties are determined by electro-steric and (partially) by electro-hydrodynamic interactions. Due to the large size asymmetry between the colloidal macroions and the small microions, the degrees of freedom of the latter can be integrated out, resulting in an effective one-component interaction potential describing microion-dressed colloidal quasi-particles.

We present a comparison, and partial extension, of various methods of calculating effective colloidal interaction parameters including effective charges and screening constants [1]. Additionally, we discuss osmotic suspension pressure calculations for dispersions in Donnan equilibrium with a salt-ion reservoir. We discuss methods including cell-models [2, 3], renormalized jellium models [4], and multi-colloid-centered mean-field models [5, 6]. The pros and cons of the various methods are assessed by comparison with primitive model based computer simulations.

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## Effects of correlation between small spheres on phase diagram of binary hard-sphere systems

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Phase behaviors have been investigated focusing on attraction distance [1, 2]. Here, we discuss binary hard-sphere systems which is a simplified model system of protein-polymer (or crowder) solution. In experiments the distance of effective attraction between proteins is changed by changing the size of the polymers.

On the other hand the interaction distance depends on the size of smaller spheres in theoretical studies. Effective attraction between large spheres appears due to the translational motion of small spheres. It is called depletion effect which is originally discussed by Asakura and Oosawa (AO) [3]. The AO potential is monotonically increase with distance  $r$ , and is zero when  $r$  is larger than the diameter of small spheres. Therefore, the correlation length is proportional to the diameter-ratio  $q$  in the AO potential. Dijkstra *et al.* studied the relation between the phase diagrams and the ratio  $q$  using computer simulations [2].

However, the AO potential is too simple for high-density systems because the correlation between small spheres is neglected in the theory. We investigate the effect of the phase diagrams between small spheres on the crystallization by using an integral equation theory with effective one component models.

The effective potential is calculated by an integral equation theory (HNC-OZ). Here, we call it IE potential. Using the IE and AO potentials, we also obtain the phase diagrams at  $q = 1/6$  and  $1/10$  by a density functional theory with thermodynamic perturbation theory. The crystal structure is supposed to be fcc and bcc crystals.

The calculated IE potentials have oscillations, and definition of correlation length is not easy due to the oscillation structures [4]. Using the IE and AO potentials, we obtained the coexistence density and drew the phase diagrams [4]. Basically the coexistence phase for the IE potential system is wider than that for the AO potential system. In particular, in the phase diagram at  $q = 1/6$  for the bcc crystal, large difference appears. We will discuss relation between the phase diagrams and the interaction potentials based on the calculated free energy curves. Our results indicate that the relation cannot be explained only by the ratio  $q$ .

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Quasicrystals are structures with long range order but missing translational symmetry. They may possess any rotational symmetry including those that are not allowed in periodic crystals. Due to additional degrees of freedom that do not exist in periodic crystals, additional hydrodynamic modes called phasons arise supplemental to the phononic modes known from periodic crystals. Phasonic excitations correspond to correlated rearrangements of the particles.

We study the development of defects close to the melting transition. It has been predicted that dislocations and disclinations cause the melting of the quasicrystal (cf. KTHNY theory [1, 2]). We observe a first order phase transition. We analyze orientational and positional correlation functions and reveal the similarities and differences of the melting process of quasicrystals in comparison to the melting of periodic crystals.

Furthermore, for low densities quasicrystals coexist with the gas phase. We study the shape of the surface as well as the dynamics of the particles at the surfaces. In addition, we analyze the growth process (cf. [3]).

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## Depletion interaction in charged colloidal systems: excluded volume and electrostatic coupling

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Neutral nonadsorbing polymers such as polyethylene glycols are used to precipitate colloidal particles including proteins from an aqueous suspension. Polymers are depleted from the region between two colloidal particles due to their random coil size, and this depletion in turn exerts an osmotic force capable of bringing colloids together. Several theoretical and experimental studies [1, 2, 3] has been conducted to address this phenomenon.

Addition of neutral polymers has two effects: i) increase of the excluded volume occupied by polymers, and ii) decrease of the dielectric constant of a suspension [4]. In real systems with charged colloids both effects apply simultaneously. However, theoretical approaches often neglect the effect of reduced dielectric constant.

Present work evaluates effects of excluded volume and dielectric constant on depletion interaction between charged collids individually using Monte Carlo computer simulations.

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## Melting upon cooling and freezing upon heating: Fluid-solid phase diagram for Švejka-Hašek model of dimerizing hard spheres

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A simple model of dimerizing hard spheres with highly nontrivial fluid–solid phase behavior is proposed and studied [1] using the recently proposed resummed thermodynamic perturbation theory for shielded attractive shell models of polymerizing hard spheres [2, 3]. The phase diagram has the fluid branch of the fluid–solid coexistence curve located at temperatures lower than those of the solid branch. This unusual behavior is related to the strong dependence of the system excluded volume on the temperature, which for the model at hand decreases with increasing temperature. This effect can be also seen for a wide family of fluid models with an effective interaction that combines short range attraction and repulsion at a larger distance (SALR models). We expect that for sufficiently high repulsive barrier, such systems may show similar phase behavior.

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## Phase transitions of the one component plasma with inverse power law interactions.

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It is presented a numerical study of phase transitions of charged particles on the plane repelling to each other via an inverse power law interaction of the form  $1/(r^n)$  for  $n = 1, 2$  and 3. Montecarlo simulations enable us to identify the expected hexatic phase for sufficiently large systems. However, finite size-scaling obtained with the aid of the multi-histogram method [3, 4] suggests a weak first order transition from fluid to hexatic phase as the coupling parameter  $\Gamma$  is decreased rather than a Kosterlitz-Thouless transition [2]. Special attention is paid for the case  $n = 2$  where double peak plots of the Binder's fourth cumulant and susceptibilities associated to different variables in terms of the coupling parameter were found in concordance with a two-stage melting transition.

Key words: Coulomb gases, solid-liquid transitions, computer simulations, finite-size systems

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# One-component log-gas: Exact Expansion of the pair correlation function for Odd Values of $\Gamma/2$

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This work is focused on the study of the two dimensional one component plasma 2dOCP, a system of  $N$  identical charged particles living in a plane and interacting among them with a logarithmic potential. This is a classical system which goes an step beyond the bidimensional ideal gas since the 2dOCP crystalizes at low temperatures or large charges. The statistical behaviour is controlled by a coupling parameter  $\Gamma = q^2/(k_B T)$  with  $q$  the particle's charge,  $T$  the temperature and  $k_B$  the Boltzmann's constant. Typically, the system is a fluid for  $\Gamma$  near to 2 and crystal arranged in a hexagonal lattice at  $\Gamma \rightarrow \infty$ . In general, the plasma is bounded in order to avoid that particles scape to the infinity because of their repelling interaction. In our case the particles may be confined with a circular box (Hard Disk) or via a harmonic radial potential (Soft Disk) generated by charging the plane uniformly with a charge  $-Nq$  which also ensures electro-neutrality.

The current work uses the approach of Vandermonde determinant to the power  $\Gamma = Q^2/(k_B T)$  expansion on the monomial functions [1, 2, 3], providing a way to study analytically the crossover behaviour from a disordered system to small crystals. It is obtained an expression for the pair correlation function which still keeps a link with the random matrix theory via the kernel in the Gaussian Orthogonal Ensemble (GOE) for odd values of  $\Gamma/2$  which enables to observe some features of the crystallization at least far from the thermodynamic limit as the coupling between particles is increased.

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## Towards a realistic description of computer-generated nano- and microgels: assembly protocol, form factors, density profiles and swelling curves of single soft particles

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Soft colloids are becoming more and more popular in the physics community. Typically, soft particles have an internal polymeric architecture, which allows them to reach very dense regimes, with large interpenetration of the polymer chains. A very interesting class of such soft building blocks comprises soft particles with tunable swelling properties and an extremely broad range of applications, the so-called microgels [1].

Despite the huge experimental interest in microgels, theoretical efforts devoted to understand microgel behaviour have thus far barely scratched the surface of the problem. Most of these have been based on simple models, such as the Hertzian model for elastic spheres [2], which completely neglect the internal polymeric nature of the particles. However, the polymeric degrees of freedom are relevant in high-density states, and thus must be taken into account for a correct description of the behaviour of the dense phases that are required by many applications. Recently, more fine-grained computational studies have investigated nanogels generated with a regular mesh, generally based on the diamond lattice [3].

In this contribution we go one step further and generate microgels out of disordered gel networks obtained by the self-assembly of tetravalent (crosslinkers) and bivalent (monomer beads) patchy particles under spherical confinement. We employ a patchy model that allows for a very fast annealing of the system which, at the end of the assembly stage, is nearly fully bonded. The resulting network topology is used to generate the initial microgel configuration, which is subsequently simulated with a bead-spring model. We investigate the structure (in reciprocal and real space) and the swelling curves of microgels of different size and crosslink concentration, and assess their dependence on the extent of the spherical confinement used during the assembly stage. To highlight the validity of the assembly procedure we design a nanogel with the same crosslinkers concentration of experimental PNIPAM nanogels, finding that the *in-silico* particle well reproduces the swelling behaviour of the experimental ones. The devised protocol will allow us to not only investigate the dependence of the microgel properties on the underlining microscopic interactions, but also to compute the effective interactions acting between multiple soft particles.

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## The Second Virial coefficient of the Mie Potential and predictions of the critical temperature for short range attractive potential fluids

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Series expansion expressions for the second virial coefficient  $b_2$  of the Mie or  $m : n$  potential,

$$\phi(r) = \lambda \epsilon \left[ \left( \frac{\sigma}{r} \right)^m - \left( \frac{\sigma}{r} \right)^n \right]; \quad m > n > 3, \quad (1)$$

for various  $m$  and  $n$  values are considered ( $\lambda$  is a numerical constant). The rates of convergence and the temperature dependence of  $b_2$  for selected  $m$  and  $n$  values are investigated. The high temperature limit series expansion of the Lennard-Jones 12 : 6 special case potential is shown to converge rapidly, even for quite low temperatures, such as  $\sim 0.05$ , whereas the low temperature expansion is shown to be an asymptotic series [1]. The contributions to  $b_2$  from the repulsive and attractive terms parts of the potential are derived. There is a very slow convergence at high temperature of the Lennard-Jones (LJ)  $b_2$  to the  $m = 12$  inverse power value. The behaviour of  $b_2$  in the  $\infty : n$  limit, which is a generalisation of the Sutherland potential,  $n = 6$ , is explored.

The Boyle temperature (BT) and maximum  $b_2$  temperature (MT) as a function of  $m$  and  $n$  are investigated. The BT is monotonically decaying and the MT manifests a minimum with increasing exponent values. The MT in the  $m \rightarrow \infty$  limit of the  $m : n$  potential diverges. Simple and accurate analytic expressions for the BT, MT and critical temperature of the  $2n : n$  potential in the region of large  $n$  are derived using the convergence to Baxter's sticky sphere model of this potential in this limit [2, 3, 4]. These data are difficult to obtain by simulation, [5] so this theory partly fills this gap in knowledge. The critical point region behaviour of the short range attractive potentials could be exploited in the fields of protein nucleation and crystal growth, and in describing the structure and kinetics of colloid aggregation and gelation. Both of these particle types can be represented approximately by the generic  $2n : n$  potential in the large  $n$  limit.

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## Morphological transition of adsorbed aggregates and micelles onto a gold surface

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In the evergrowing field of nanotechnology, metallic nanoparticles have a great potential for applications ranging from optics to biomedicine [1]. In this context, colloidal science finds widespread applications in our understanding of nanoparticle behavior and synthesis. Particularly, the colloidal preparation of metallic nanoparticles in solution is often mediated by surfactants that can adsorb and aggregate readily on their surface [2].

Yet, our understanding on the structure and function of these aggregates remains very limited. In the preparation of gold nanoparticles, for example, coating of the surface by the cationic surfactant cetyltrimethylammonium bromide (CTAB) not only serves as a stabilising agent against aggregation, but also is believed to have an important role in determining growth rates and particle shape [3].

In this paper, we study the structure of CTAB coatings on gold surfaces using Molecular Dynamics simulations. Firstly, we have used quantum density functional theory and Møller-Plesset perturbation theory in order to develop a state of the art force field for the CTA<sup>+</sup> cation. The new model is employed in simulations with the Gromacs package, using SPC water as a solvent.

In our study, we focus on the structural changes that occur on the surface of gold as a function of surfactant number, and also consider the role played by ionic force and the presence of co-surfactants and additives. Our results reveal a very rich behavior of the adsorbed surfactants, which ranges from the formation of stable dimers, to small aggregates or micelles, as well as fully developed bilayers depending on the conditions.

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The square-well potential (SW) is a simple model that can reproduce with accuracy the behaviour of real single component fluids. Due to its mathematical simple expression, this model is useful to prove the efficiency of approximation theories proposed in statistical mechanics, besides has been a main ingredient to study complex fluids (DPT [1][2], SAFT-VR [3][4]). However, the SW short range potentials have not been studied well enough, their vapour-liquid phase diagrams appear inside the fluid-solid transition, making them difficult to study [5][6]. These ranges are important because they can be used in the description of colloidal suspensions. An example of an important application is the description of the liquid-liquid phase separation of the  $\gamma$ -crystallins, a family of monomeric lens proteins [7]. In this work we propose an expression for the Helmholtz free energy as a function of density, temperature and the SW parameters for a fluid represented by a square well potential with short range interactions using data from numerical simulations in the microcanonical ensemble [8].

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## Transitions between ordered and disordered phases of patchy particles in two dimensions

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We consider a two dimensional ensemble of patchy particles that carry up to two patches: while the particles themselves are impenetrable we assume for the patch-patch interaction a Kern-Frenkel type potential [1]. We fix the density to close packing conditions; thus particles form a hexagonal lattice and we are left with the orientational degrees of freedom. Investigations on the system have been carried out with standard Monte Carlo simulations, with ensemble sizes ranging up to 83 000 particles.

We have first analysed the bonding patterns that one-patch particles are able to form at vanishing temperature (see also [2]). Depending on the opening angle of the patch we have identified in total seven characteristic bonding patterns and have classified them in terms of regular tilings, formed by the connecting lines of bonding particles. We have then increased the temperature systematically for the one- and the two-bond cases and have investigated how the orientational order of the ground state configuration changes upon the temperature change. In an effort to quantify the findings of these investigations we have introduced suitable order parameters. Data are compared with existing experimental results [3].

We also present results for the configurations that particles are able to form in case they are decorated by an asymmetric arrangement of two patches: these arrangements are the result of a trade-off of energetic and entropic contributions to the free energy and turn out to show a rich wealth of structural morphologies.

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Diffusion of Brownian particles in random potential energy landscapes (PELs) is encountered in many situations, including the transport through inhomogeneous bulk materials, such as porous media, gels, rocks, living cells, and biomembranes, as well as in models of the glass transition and protein folding [1, 2].

We experimentally realise random potential energy landscapes. While strongly focussed light (optical tweezers) can be used to trap a colloidal particle, we broaden this concept to extended light fields, namely one- and two-dimensional speckle patterns, by using a spatial light modulator [3] or a diffuser [4].

Two-dimensional colloidal layers are exposed to these PELs, which can be time-dependent or constant, and simultaneously monitored by video microscopy. The dynamics of the particles in PELs, e.g. their mean-square displacements, exhibit a subdiffusive behaviour in most situations [1]. However, depending on the characteristics of the PEL and the particle concentration also other dynamics is found. For example, time-dependent PELs can lead to enhanced diffusion. In concentration series, moreover, counter-intuitive behaviour is observed, namely faster diffusion in more concentrated suspensions. Binary mixtures in static PELs can result in obstructed motion. The different behaviour will be presented and the underlying physics discussed.

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## The Constant Force Continuous Molecular Dynamics for potentials with multiple discontinuities.

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In this work we present an extension of the Constant Force Approach [1] to the case of potentials with multiple discontinuities. To test the method we selected the square-well potential of range  $\lambda = 1.5$  that exhibits two discontinuities and some cases of the square-well plus square-shoulder potential with three discontinuities. Square-well single phase properties, vapor-liquid phase diagram and surface tension were calculated and compared with available simulation data. Besides, we analyzed the internal energies of a square-well plus a square-shoulder potential. For both potentials a good agreement has been found when compared with results of other simulation techniques (Discontinuous Molecular Dynamics and Monte Carlo methods). This extension can be easily implemented to more general and efficient continuous molecular dynamics packages (HOOMD, GROMACS, NAMD, etc.).

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# The effect of Brownian fluctuations on the behaviour of self-orienting dumbbell particles driven by an external flow in a microchannel

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Suspended particles moving in a fluid generate a flow disturbance and, as a consequence, move in response to the flow field. Hence, colloidal particles are coupled via hydrodynamic interactions (HIs). This effect becomes even more interesting in geometrical confinement, where it can drive spatial organisation of microparticles, according to the geometry of the particle. Therefore tailoring the particle's shape becomes a powerful tool in order to have spatial control over the system [1, 2].

We study the system composed of a dumbbell particle dragged by the fluid flow in geometrical confinement (quasi 2D system). Our simulations are inspired by the experimental work that have been performed on a microfluidic device [1]. The authors show that it is possible to predict the trajectory and orientation of the particle inside the channel, given the shape of the particle and the geometry of the channel. As a consequence, it is possible to tailor the shape of the particle in order to have control over its position. This simple system already exhibits a large variety of behaviour which is governed by the HIs of the particle with itself and with the boundaries of the channel. In our study we focus on the hydrodynamic self-interaction of the dumbbell, which is mainly responsible for the self-orientation of the particle along the direction of the fluid flow.

Previous works have been performed at very high Péclet numbers, but an investigation at low Péclet numbers is still missing. We perform numerical simulations with Molecular Dynamics and Stochastic Rotation Dynamics techniques [3, 4] to investigate the system at different hydrodynamic regimes: increasing the relative strength of diffusive against convective transport we can progressively enhance the thermal noise and observe the response of the particle in the process of self-orientation. We draw a state diagram which qualitatively describes how well the particle can self-orient as we tailor the particle's shape and tune the Péclet number.

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The phase behaviour of a liquid crystalline system may be modified by the addition of a second component, introducing the density of the additive as a new parameter with which to tune properties. It is known from simulations [1] and experiments with rod-like colloidal viruses [2] that the binary mixture of hard spherocylinders and hard spheres shows a rich phase behaviour, including the binary smectic ( $\text{Sm}_2$ , or *lamellar*) phase with spheres occupying the interstices between layers of rods. In this work, the formation of the  $\text{Sm}_2$  phase in gravitational and spherical confinement was studied in a system of short range repulsive spherical and rod-like fluorescent silica particles as it approached equilibrium [3]. Particle fitting algorithms were used to extract the positions of the particles and the orientations of the rods from confocal image volumes [4]. This allowed the study of the growth and equilibrium structure of the  $\text{Sm}_2$  phase at the single particle level [5].

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# Universal self-assembly of one-component three-dimensional decagonal and dodecagonal quasicrystals

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Quasicrystals (QCs) have been experimentally observed for both metallic alloys and soft matter systems that suggests a common microscopic mechanism of QC formation. Stability of three-dimensional (3D) one-component QCs has been predicted using density functional theory and then confirmed by molecular dynamics simulations. The general idea explaining QC formation is the existence of two or more interparticle length-scales. This idea is supported by the fact that effective interactions for metallic alloys and soft matter systems are often described by multi-length-scale potentials.

A general problem of computer simulation of 3D QCs is the lack of simple geometrical criteria of QC formation. So, to localize numerically the QC phase, one should usually simulate over a wide range of system parameters [1]. We show how to universally localize thermodynamic parameters where decagonal and dodecagonal QC order may appear for a given particle system. We suggest that the formation of such QCs from the fluid phase is mostly determined by the values of two dimensionless structural parameters of the fluid. The parameters reflect the existence of two effective interparticle distances (bond lengths) originated from two-length-scale nature of interaction potential. These are the ratio between effective bond lengths,  $\lambda$ , and the fraction of short-bonded particles  $\phi$ .

In order to verify this idea, we use different two-length scale potentials: oscillating pair potentials which mimic oscillating metal interactions, purely repulsive potentials corresponding to core/shell model of colloids and the embedded-atom model potential for aluminum. The values of effective parameters which favor either decagonal or dodecagonal order are respectively determined from system with RSS potential and Dzugutov potential for which formation of corresponding 3D QCs have been firstly observed [2, 3]. Adjusting the states of other two-length scale systems to obtain the same values of effective parameters, we observe self-assembly of the same QC phases at cooling.

Our results suggest that mechanism of both decagonal and dodecagonal QC formation is universal for both metallic and soft-matter systems and it is based on competition between interparticle scales.

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When crystals are (super)heated close to or beyond their melting point, their behavior becomes strongly influenced by the fluctuations of the particles around their lattice sites. These fluctuations lead to the spontaneous creation and destruction of defects in the crystal, facilitate diffusion of particles and defects, and reduce the resistance of the crystal to external strain, lowering its elastic constants. The degree to which a crystal can be superheated under ideal conditions is limited by the Born stability criteria: the elastic constants for all strain directions must remain positive [1]. Breaking this criterion leads to an immediate melting of the crystal due to large-scale fluctuations, rather than the more typical nucleation-and-growth or edge-melting scenarios.

Here, we explore this melting scenario in simulations of colloidal particles interacting via screened Coulomb repulsions. Recent experiments have shown that these soft interactions lead to particularly strong fluctuations in crystals close to melting, which strongly impact the stability of the crystal [3]. At high densities, these particles form face-centered cubic (FCC) or body-centered cubic (BCC) crystals, depending on the degree of electrostatic screening. Upon either heating or diluting these crystals, we find that the two crystals behave differently. The FCC phase loses its rigidity via a similar route as e.g. Lennard-Jones crystals [2], where the elastic constant associated with a specific shear direction decreases to zero. Surprisingly, in the BCC structure this scenario appears to be avoided, and the weakest elastic constant approaches a small but finite value, suggesting a qualitatively different melting scenario. We systematically explore the elastic constants of both solid phases in detail, and quantify their behavior close to the melting temperature. Additionally, we investigate the large-scale collective fluctuations that appear in the superheated regime [2, 3].

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We present an optically driven colloidal microscopic rheometer based on the recent work of Williams et al. [1]. With optical tweezers, we create a colloidal corral that confines a highly packed system of particles. In addition, we introduce an inner triplet of superparamagnetic particles which we can drive by applying an in plane rotating magnetic field. The interplay between magnetic and optical forces allows us to experimentally build a two dimensional Taylor-Couette cell, in which the outer wall and inner wall move independently of each other. Such a system can be used to explore the rheological properties of confined colloidal suspensions at a microscopic scale. The small scale of this rheometer allows us to explore how deformations in the structure lead to shear thinning, and how the coexistence of ordering phases leads to depinning transitions. Despite the discrete nature of the system, we observe local instabilities in the response of the layer's flow to the applied shear, which is a characteristic of shear banding in larger systems. Besides the rheological phenomena, we believe that these type of experiments can be useful to develop the understanding of non-equilibrium many body systems.

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## Self-assembly of patchy nanoparticles with various patch arrangements using molecular simulation

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We investigated the phase diagram of self-assembled Janus nanoparticles confined in two-dimension using a computer simulation. Self-assembly is involved in various functional materials that are widely used in industry and there is a strong relationship between self-assembled structures and specific functions. One general method for controlling the morphologies of self-assembled nanoparticles is designing colloidal particles with anisotropic shapes and chemical interactions. Recently, anisotropic nanoparticles with complex surfaces and shape can be synthesized. Here, Janus nanoparticles have received much attention because of their characteristic physical properties that are due to more than two distinct chemical or physical surfaces. Therefore, diverse morphologies of self-assembled patchy nanoparticles have expected to be obtained by designing the Janus nanoparticles. In a recent study, it is known that Kagome and hexagonal crystals are found at low and high pressure using a triblock patchy nanoparticles [1]. However, to our knowledge, there has been no study that tried to investigate a phase diagram of self-assembled structures in a different design of the patchy nanoparticles. In our simulation, we found various self-assembly structures depending on a different design of the patchy nanoparticles. Our simulation offers a guide to qualitatively predict the self-assembled structures of the patchy nanoparticles based on a different design of that.

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## **Topic 6**

# **Films, Foams, Surfactants, Emulsions**

## Effect of molecules which have a core and an alkyl chain on lipid bilayers

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Small organic molecules in biomembranes control the physico-chemical property of phospholipid bilayers. However, these effects have not been clarified systematically. The bilayers have a phase transition from the ordered gel phase to the disordered liquid-crystalline phase at  $T_m$ . Cholesterol disturbs the molecular order in the gel phase and lowers  $T_m$  [1] whereas *n*-alkanes enhance the molecular packing in the gel phase and raise  $T_m$  [2]. These imply that the effects of additive molecules are classified by the molecular shape, since cholesterol is rigid and core-like whereas *n*-alkanes are linear and flexible.

In the present study, we investigated the effects of various linear chain molecules, and molecules containing a core part and an alkyl chain. The effects of linear chain molecules, C14-X (X = Br, Cl, COOCH<sub>3</sub>, SH, OH, COOH, PO<sub>3</sub>H<sub>2</sub>, NH<sub>2</sub>), are found to be comparable to those of *n*-alkanes, i.e., as C14-X content increases the molecular packings in the gel phase are enhanced by similar extents to the cases of *n*-alkanes, and the  $T_m$  increases. *n*CB (4-*n*-alkyl-4'-cyanobiphenyl, *n* = 0-8: alkyl chain length) were used as the molecules which contain both of a core part and an alkyl chain. All *n*CB lower  $T_m$ . The longer the alkyl chain length *n*, the smaller the extent of the lowering. The dependence on the alkyl chain length indicates that the effect of the core part of *n*CB was cancelled on elongating the chain. The effect of *n*CB on the transition behavior between two kinds of gel phases (pre-transition) also indicated the competition of the effects of the core and the chain. These results suggest that a rigid core part and an alkyl chain in a single molecule also have contrasting effects on the phase behavior of the DPPC bilayer [3].

These findings suggest the possibility to classify the effects of additives on a phospholipid bilayer by focusing on each effect of a core and a flexible linear chain.

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## Influence of formulation on the oxidative stability of water-in-oil emulsions

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The health benefits of polyunsaturated fatty acids (PUFA) from the n-3 series leading to PUFA enrichment in various foods and nutraceuticals are widely recognized. However, because these PUFA are extremely sensitive to oxidation, precautions have to be taken in the formulation, processing and handling of such products to avoid oxidation. Lipid oxidation may generate off-flavors, rancid odors and molecules that can be harmful to health [1]. Several factors are known to promote lipid oxidation like oxygen, light, heat, transition metal ions, lipid dispersion state... that have to be controlled during food processing and storage. In this context, lipid oxidation was followed by measuring the content of primary oxidation products, for lipids in bulk phase and in water-in-oil emulsions. Different edible oils were chosen for their contents of  $\alpha$ -linolenic acid (18:3 n-3). Emulsions were formulated at varying polyglycerol polyricinoleate (PGPR)/distilled monoglycerides concentration ratios (surfactant ratio), with or without the presence of pro-oxidant metals or chelators in the internal aqueous phase. In all experiments, the aqueous volume fraction (40%) and the droplet mean diameter (1  $\mu$ m) remained constant. Besides this study, an innovative and rapid method based on differential microcalorimetry was developed for monitoring the kinetics of lipid oxidation [2]. The oxidability of the studied oils was related to their content in  $\alpha$ -linolenic acid according the following order: linseed oil > camelina oil > rapeseed oil > olive oil. The rate of lipid oxidation increased with the iron sulfate concentration in the internal aqueous phase. The iron valence or its substitution by copper had no significant impact on the oxidation kinetics. However, both chemical nature of the counter ion (molecular weight, chelating force) and proportion of PGPR surfactant used to stabilize the emulsions were influential parameters [3]. In general terms, our results suggest that surfactants at the water-oil interface do not prevent pro-oxidant species to interact with lipids in the continuous phase but that their organization at the oil/water interface is a key parameter for controlling lipid oxidation.

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**A conductimetric study of alkyl carboxylate surfactants as a function of length chain, counter-ions and temperature. Interpretation below and above the critical micellar concentration using a transport theory.**

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High precision conductivity experiments were performed on long-chain carboxylates: sodium octanoate (NaC8), sodium decanoate (NaC10), potassium decanoate (KC10), caesium decanoate (CsC10) and sodium dodecanoate (NaC12) in aqueous solutions and at temperatures from 5°C to 55°C in step of 10°C [1]. Concentration range was chosen to cross the critical micellar concentration (cmc) and to cover the pre- and postmicellar range.

We present an interpretation of experimental results in the frame of a combination of Smoluchowski equation for the dynamics and the mean spherical approximation (MSA) for the equilibrium pair distribution function [2].

Below the cmc one highlights premicellisation reactions of the system and above the cmc we obtain the effective charge of the formed micelles and then quantities of adsorbed cations.

We finally discuss about specific and temperature effects below cmc in term of ion pairing and above cmc in term of micelle formation.

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## Theory of spreading and contraction behavior of benzene drop on water

6.004

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Spreading of one liquid over another is the process, which is important for biological systems as well as for many applications in the fields of pharmaceuticals, coating deposition technology, oil spills, food industry and many others. When a droplet of organic liquid with low surface tension is placed on the surface of aqueous medium with which it has low mutual solubility, the decrease in surface energy of the considered system results in partial or complete spreading of organic liquid. However, in many cases the initial spreading of a droplet of top liquid is followed by its contraction into a lens. We have analyzed spreading and contraction behavior for benzene drop on the top of water. In our theory such behavior is attributed to water dissolution in benzene. Although saturated concentration water in benzene is as small as  $2.5 \cdot 10^{-3}$  it significantly changes surface forces in thin benzene film surrounding the droplet and thus affects the wetting behavior. On the basis of well-known equations for dispersion forces and electrostatic interactions of water molecules with film boundaries and with each other, as well as originally developed equations for interaction of water molecules in film with discrete charges adsorbed on water-benzene interface we estimated excess free energy, obtained isotherms of water adsorption in benzene film and the total isotherms of disjoining pressure in film. The results indicate that gradual dissolution of water in benzene plays essential role in spreading and contraction phenomenon, while all image forces and dispersion forces, as well as hydrogen bonding between adsorbed water and aqueous substrate are important and should be accounted for.

## Ultra-slow dynamic surface tension of surfactants induced by salts

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Dynamic surface tension (DST) is an important property of surfactants in the processes where the time-scale of the wettability of the liquid is crucial. For example, time-dependence of wettability is of crucial importance for the effective spreading of pesticides on the leaves. Similarly, its understanding is also important in the textile, metal and cleaning product manufacturing industries[1]. Since the presence of salts is ubiquitous, in many instances surfactants encounter different kinds of salts or sometimes salts are deliberately added to modify the surfactant properties. However, little is known on the effect of high salt concentration on the behavior of surfactants solutions.

We investigate the influence of salt concentration on the dynamic surface tension property of water soluble surfactants using pendant drop method and Sum Frequency Generation spectroscopy (SFG). The latter, allowed us to probe the fast molecular dynamics and transient phenomena at the air/liquid interface.

We have studied the behavior of two types of surfactants: the cationic CTAB and the non-ionic Tween-80 solutions up to very high NaCl concentration (6 M). Our results show that the time-scale of dynamic surface tension of both ionic and non-ionic surfactants is greatly increased by the addition of salt. Moreover, the surface excess concentration,  $\Gamma_{eq}$  decreases for the cationic CTAB surfactant by increasing salt concentration. The kinetics of CTAB adsorption at air/liquid interface measured by SFG corresponds well to the ultra slow dynamic surface tension at high salt concentration and reveals a less ordered monolayer at the interface at short time scale. We deduce the mechanism of surfactant transport by drawing the relationship between characteristic time,  $\tau$  (time required by surfactants to decrease the surface tension to half of the total surface tension decay), and the bulk concentration of the surfactant[2]. For the non-ionic surfactant, Tween-80, the electrostatic interactions do not play a significant role and therefore the adsorption kinetics can be well described by diffusion-controlled model. Surprisingly, for the cationic surfactant CTAB, the mechanism of surfactant transport to the interface in the presence of salt does not appear to be diffusion controlled. Our results show that the increase of ions concentration in the solution create an adsorption barrier which prevents the adsorption of CTAB monomers at the interface and thereby increases the timescale of the DST decay. We discuss the processes which may explain such adsorption dynamics.

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## Stabilization of food-grade oil-in-water emulsions by chitosan-modified nanoparticles as a function of pH

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Particle-stabilized emulsions are desired in the food industry due to their long-term stability and surfactant-free character. In this work, a novel edible stabilizer has been demonstrated to produce ultrastable oil-in-water emulsions consisting of micron-sized droplets via high-pressure homogenization [1].

Here, stabilizer particles are produced by modifying non-covalently silica nanoparticles with a weak polyelectrolyte, chitosan. Chitosan-modification increases the particle hydrophobicity, thus enhances particle adsorption at the oil-water interface. The adsorption of chitosan to silica nanoparticles is reversible and strongly depends on the pH of the continuous phase, which significantly influences the emulsion stability. Confocal microscopy, cryo-scanning electron microscopy, diffusing wave spectroscopy, and bulk and interfacial rheology are used to shed light on different stabilization mechanisms. We have found that particle modification at different pHs lead to distinct microstructures and macroscopic behaviors for the emulsions. This provides a versatile system that can result in either a network or a Pickering stabilization by simply tuning the pH. Furthermore, we have demonstrated that the pH change, performed at different stages during the production of the emulsification, do not induce any changes in the final product, which is industrially important due to potential practicalities such flexibility may provide.

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## Outstanding stability of free-standing co-polymer films above the glass transition – an interfacially-driven micro-phase separation

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Thin films of polymer melts - wherein the flow occurs under the confinement of submicrometric dimension - span a broad range of industrial processes as well as natural phenomena. The drainage dynamics and stability of such films puts forward many fundamental questions and has been investigated extensively in last few decades. Most polymer melts make very unstable films above their glass transition. However, in a recent work we have discovered that certain statistical PDMS-g-PEG-PPG block-copolymer (DBP) melts can make large ( $> 10 \text{ cm}^2$ ) and extremely stable, free-standing thin films (15 – 100 nm thickness) far above the glass transition and without the addition of stabilising agents.<sup>1</sup> Fig. 1 shows the temporal evolution of interference pattern of a vertical film draining under gravity. The film reaches a thickness of roughly 30 nm before rupture. Interestingly, we also observe a layer-by-layer thinning (stratification) for vertical as well as horizontal films, which can be correlated with a characteristic length scale of  $\sim 15 \text{ nm}$  of the *isotropic* bulk melt, as shown in Fig. 2. The above observation suggests that structural forces play a major role, and put forward many open questions such as, role of molecular structural parameters (backbone and side chain lengths, chemical composition and statistical distribution of the side chains, chain flexibility etc.), and exact interfacial ordering of the polymers in the vicinity of melt interface. Hence in order to get the complete picture we have obtained 12 different derivatives of DBP (supplied by EVONIK), where the structural parameters are systematically varied keeping the chemical architecture same, have planned to approach the underlying stability mechanism from different paths using various complementary experimental techniques: interfacial rheology, interfacial tension, time-dependent vertical and horizontal film-pulling experiments. Furthermore thinning via discrete steps also suggests two possibilities: either a *simple confinement effect*, or an *interfacially driven micro-phase separation*. However our recent experiments associated with film life-time dependency on exposure time and height of the film guide us to believe in later hypothesis. Hence in order to confirm more direct characterization of interfacial organisation we have we have also planned high-quality X-ray reflectivity and GISAXS at SOLIEL. We are also interested in theoretical modelling which can account for such interfacial organisation and can explain so long term stability (the associated drainage dynamics) and stratification observed experimentally. We believe that our investigations will provide deep insight about the understanding the stability of polymeric thin films, foams, and emulsions without the use of stabilizing agents.

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## Surface and interfacial activity of pH-responsive surfactant-free amphiphilic Janus nanoparticles

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The ability of amphiphilic Janus nanoparticles (JNPs) to partition at the liquid-liquid and air-liquid interfaces can be especially attractive for a plethora of new applications. Unlike molecular surfactants or homogeneous nanoparticles, the JNP could act as carriers of different small molecules/actives or bulk-like properties, magnetic, optic or electric without a dramatic effect on their ability to partition at interfaces. The interfacial activity of the JNPs at air-water interfaces, although hypothesized, has not been yet directly demonstrated, mainly due to the difficulty of synthesizing scalable amounts of such materials in surfactant-free conditions. We have previously reported the synthesis and polarity reversal within a homologous series of JNPs in surfactant-free conditions.[1] Here we demonstrate for that surfactant-free JNPs with tunable polarity balance can partition at both air-water and liquid-liquid interfaces. The polarity balance of the JNPs can be tuned by the pH such that the amphiphilicity is switched on or off, at low or higher pH values, respectively. Upon adsorption of these JNPs at the oil-water interfaces, the particle-laden interface acquires the pH-responsiveness functionality. For example Pickering emulsions obtained with the above JNPs undergo a reversible w/o to o/w dynamic phase transition depending on the pH of the aqueous phase. In contrast to homogeneous nanoparticles (HNPs), we also show that the JNPs show an enhanced ability to partition at interfaces. This demonstrates that the JNPs can be regarded as the next generation of amphiphiles.

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## Photoregulating the self-assembly of lipophilic guanosine derivatives at the air-water interface

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Basic blocks of DNA are very interesting constituents for designing supramolecular single-layer and multilayer surface architectures. Our recent studies of self-assembly of nucleoside derivatives in monolayer films at the air-water interface (Langmuir films) reveal that guanosine derivatives exhibit very different behaviour from analogous derivatives containing other nucleobases [1]. We also demonstrated that the number of lipophilic chains attached to the sugar hydroxyl groups and the type/concentration of ions present in the water subphase strongly affected molecular organization of guanosine derivatives in Langmuir monolayers as well as in Langmuir-Blodgett (LB) films deposited on various solid substrates [2,3,4]. Modifications of these parameters hence provide a possibility of tuning intermolecular organization in thin film configurations.

An appealing strategy for control and manipulation of intermolecular organization is to use optical irradiation. To test the applicability of this method in case of guanosine derivatives we investigated Langmuir films of azo-functionalised guanosine molecules in which the isomerisation can be switched from trans to cis and vice versa by irradiation with UV and visible light. Photoinduced modifications within Langmuir films were studied by film balance experiments and by Brewster angle microscopy (BAM). We were able to reversibly induce changes in the surface pressure of the film by alternately irradiating with UV and blue light, indicating a light-induced change in the film structure. We also investigated effect of optical irradiation on binding properties of the film for different compounds added either to the water subphase or to the air-water interface.

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## When is a surface foam-phobic?

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By integrating the Young-Laplace equation including the effects of gravity, we have calculated the equilibrium shape of the two-dimensional Plateau borders along which a vertical soap film contacts two flat, horizontal solid substrates of given wettability. We have found that the Plateau borders can only exist if the values of the Bond number  $Bo$  and of the contact angle  $\theta_c$  between the Plateau border and the substrate lie within certain regions in  $(\theta_c, Bo)$  space. For values outside these regions, the substrates cannot support a soap film. In other words, on a substrate of a given wettability (i.e., liquid contact angle), only Plateau borders of a certain range of sizes can form. Our conclusions are validated by comparison with both experimental and numerical (Surface Evolver) data. We conjecture that this result will hold, with slight modifications, for non-planar soap films and bubbles, and therefore that solid substrates can be used to sort bubbles of different liquid contents. Our results are also relevant to the motion of bubbles and foams in channels, where the friction force of the substrate on the Plateau borders plays an important role.

# Formation of long thread-like micelles and association of functionalised nanoparticles: A large-scale molecular dynamics study

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The driving force for the association of amphiphiles is the hydrophobic effect, which leads to an increase in the entropy due to the disruption of the hydrogen bonding network in liquid water. However, when the amphiphilic species are charged, their self-assembly is influenced as well by electrostatic forces between charged particles. The balance between two counteractive forces, namely hydrophobic effect and electrostatic repulsion between charged headgroups, determine the existence, shape and size of the aggregates.

It has been experimentally observed that the presence of different geometric isomers of the hydroxybenzoate (HB) anion leads to different shapes and size of dodecyltrimethylammonium chloride (DTAC) micelles. In the presence of the 2-hydroxybenzoate long thread-like micelles emerge, while in the presence of 4-hydroxybenzoate only spherical aggregates were observed [1]. Our simulation studies of the structure and stability of long cylindrical DTAC micelles in the presence of HB salts revealed that it is the interaction of the 2-HB with DTAC, which is the cause of the difference [2, 3].

We recently performed large-scale molecular dynamics simulations (of up to 1.5 million particles) of the spontaneous micellisation of DTAC in the presence of HB and observed large structures comprising more than 1000 DTAC unimeres which are the result of the fusion of several smaller initially spherical micelles. Several micellar fusions were facilitated by the hydrogen bond formation between HB anions incorporated into the participating micelles. In this contribution, we will discuss the role HB anions play during the formation of these structures.

Expanding on earlier work in our group [4], we also performed large-scale molecular dynamics simulations of gold nanoparticles functionalised with hydrocarbon chains having neutral or charged termini. Interestingly, we observed that also the nanoparticles with charged termini tend to associate to form dimers and even higher aggregates of almost linear shape, when the carbon chain contains more than 18 atoms. In this contribution, the structure of aggregates and the bunching of the carbon chains, which makes their formation possible, will also be discussed. Finally, the similarities and differences between the self-assembly of the micelles and the nanoparticles will be analysed.

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## What determines the value of the surface tension at the critical micelle concentration?

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It is well-known that the addition of a surfactant to a liquid decreases the value of the liquid's surface tension significantly. This phenomenon forms the basis of several oil recovery schemes and has (therefore) been the subject of extensive experimental, simulational and theoretical work. Key in any theoretical description is the Gibbs adsorption equation which relates the slope of the decrease in surface tension to the amount of surfactant adsorbed at the interface. Somewhat counterintuitively, it predicts a constant decrease with the logarithm of the surfactant concentration even when the structure (adsorption) of the surfactant-laden interface itself remains constant. The decrease in surface tension with surfactant concentration abruptly ends at the critical micelle concentration when the surfactants in the bulk liquid reorganize themselves in micelles. The surface tension at which this occurs, the lowest achievable surface tension, is a key quantity of interest. In this work we investigate theoretically the factors that determine its value by combining the Gibbs adsorption equation with the mass action model and show how it is consistent with experiment.

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Aqueous foams are an important model system that display coarsening. Coarsening in dispersions and foams is well understood in the dilute and dry limits, where the gas fraction tends to zero and one, respectively. Ostwald ripening type of process can be observed in liquid foams, while in the dry limit the average size of the bubbles follows a power law with exponent close to 0.5. However, there is an intermediate state where the foam undergoes a jamming transition from a fluid-like to a solid-like state at a critical gas fraction,  $\phi_j$ . The coarsening dynamics in this limit is not fully investigated. Also, the influence of coarsening on the mechanical response in this state, if any, remains poorly understood.

Here, we probe coarsening and mechanical response using numerical simulations of a variant of the Durian bubble model for wet foams [1]. As in other coarsening systems we find a steady state scaling regime with an associated particle size distribution. We relate the time evolution of the coarsening process to the wetness of the foam and identify a characteristic coarsening time that diverges approaching jamming. We further probe the mechanical response of the system to strain while undergoing coarsening. There are two competing time scales, namely the coarsening time and the mechanical relaxation time. We relate these to the evolution of the elastic response and the mechanical structure.

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The formation of self assembled structures such as micelles and vesicles has been intensively studied and is well understood. Recent studies [1] use a new approach of vesicle formation by starting with a molecular frame (based, e.g., on DNA) which serves as the basis of new micelles/vesicles. In this way (i) shape and size of the desired micelle/vesicle can be predefined, e.g., by using ellipsoidal rather than spherical molecular frames, and (ii) the ability to generate regularly shaped vesicles can be enhanced.

While the self assembly of micelles/vesicles is relatively well understood, the frame-guided assembly process has not yet been explored in depth from a theoretical perspective. We developed a theoretical model of the frame and the amphiphilic molecules which via Monte Carlo simulations can be analysed to obtain information about the driving forces and the kinetic properties of micelle/vesicle formation. Via optimized simulation routines very large systems can be handled in order to be close to the typical sizes, relevant for the experimental situation.

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## The non-equilibrium surface growth of anisotropically interacting patchy particles

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Understanding the non-equilibrium growth process of patchy particles like colloids with metal patches or organic molecules on organic/inorganic substrates requires careful consideration of anisotropic interactions among the particles [1, 2]. One needs to establish reasonable coarse-graining of the system to model anisotropic interactions in order to reduce computational effort while keeping the system realistic at the same time. In order to get a fundamental understanding of such systems, we investigate the influence of interaction anisotropy among particles/molecules on the shape of clusters in the submonolayer growth regime. The diffusive motion of single molecules on organic and inorganic substrates can be highly restricted due to the charge pattern of electrostatically heterogeneous surfaces [3, 4]. This results in direction-dependent thermal activation energy barriers for adsorbed molecules. We perform kinetic Monte-Carlo simulations on a highly coarse-grained level to study the early stage of thin film growth for both, interaction and diffusion anisotropy.

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# Pattern Directed Hierarchical and High-Aspect-Ratio Micro/Nano-Structures on Thin Viscoelastic Films Experiencing Contact Instability

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Fabrication of mesoscale structures by self-organization of thin films undergoing contact instability have been explored theoretically [1 – 3] and experimentally [4,5], for their wide range of applications alongside their appearance in many interesting scientific phenomena. In particular, adhesion and debonding of the thin viscoelastic solid films [3], with a surface, namely the contactor, has been employed as a model prototype to study the different features of the contact instabilities. Especially, the patterns fabricated by the contact instabilities of the thin films on the contactor is found to have a very significant influence on the adhesive properties of the polymeric materials. In this direction, one very important aspect is found to be the use of the contactors with periodic physical or chemical patterns, which enforce a lateral variation of wettability gradient to engender a large area ordering to the otherwise randomly distributed patterns. Herein, with the help of three-dimensional nonlinear simulations, we unveil some interesting aspects of the pattern directed debonding of adhesive viscoelastic films. We show that the viscous or elastic compliances of the viscoelastic film and the speed of the contactor play pivotal roles in causing distinctive transitions in the modes of debonding – peeling, catastrophic, and coalescence [6]. Further, unlike a homogeneous contactor [6], the patterned contactor allows better resilience in modulation and control of the pattern morphology to impose complexity and increase the elevation of the structures. In addition, use of the patterns on the contactor enable the fabrication of high aspect ratio polymer patterns, patterns with nanoscale periodicity, and hierarchical patterns, among others. The results shown can be of significance in the fabrication of superhydrophobic surfaces, MEMS, lab-on-a-chip devices, and soft lithography such as LISA.

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## **Topic 7**

# **Confined Fluids, Interfacial Phenomena**

## PYTIM: a Multi-Platform Software Package for Molecular Surface Analysis

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We present a software package for the analysis of interfacial properties of molecular systems in computer simulations. The package includes a new python implementation of tools such as ITIM[1], GITIM[2], and the Willard-Chandler method[3], for the calculation of interfacial molecules, molecular surfaces, intrinsic profiles, and layer-by-layer properties, and includes already routines for the calculation of several surface properties. The code is based on MDAnalysis[4], and as such it can natively read several of the most common trajectory formats (CHARMM, NAMD, LAMMPS, GROMACS, AMBER, DLPOLY,...). The core features, implemented using numpy, scipy or directly in Cython, are vectorized and parallelized, so PYTIM is fast: the planar interface identification scales linearly for systems up to 10,000 atoms, and  $\sim O(N^{1.3})$  up to 100,000 atoms. On a 1,7 GHz Intel Core i7, the surface identification for a system of 10,000 atoms requires only 0.2 s. Among other features, PYTIM can handle liquid/vapour, liquid/liquid interfaces and systems with partial miscibilities. PYTIM can be used as a python library or as a stand-alone program. PYTIM is open source and freely available on github and on the Python Package Index (pypi).

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## Distribution of the surface tension along the interface normal in various liquids

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At the molecular level, surface tension arises as a consequence of the imbalance of intermolecular forces at the interface. In the case of liquid-vapor interfaces far from the critical point, the interfacial molecules lack practically any kind of interactions with the vapor phase. This spatial imbalance in the attractive forces affects not only the first molecular layer, but also the immediate subsurface layers. Based on this picture, the following question arises: how does the interface and the subsequent subsurface layers contribute to the surface tension of the liquid?

To investigate this, the tangential pressure profile across the liquid-vapor interface has been calculated for five molecular liquids, namely acetonitrile, acetone, CCl<sub>4</sub>, methanol and water by the means of molecular dynamics simulations using a recently developed method [1].

Since the surface tension is directly related to the integral of the tangential pressure profile, the results can be interpreted as the distribution of the surface tension along the surface normal direction either with respect to the Gibbs dividing surface or the capillary wave corrugated intrinsic surface. Furthermore, a layerwise contribution can be obtained with the aid of the Identification of Truly Interfacial Molecules (ITIM) analysis [2]. The results clearly show that at least 85% of the value of the surface tension comes from the first molecular layer of the liquid in every case, while the total surface tension is distributed in a 0.5 - 1 nm wide range along the interface normal. Moreover, 10% contribution comes from the second interfacial layer, with the exception of methanol, where the total surface tension can be accounted for by the first molecular layer. In every case, the third and subsequent layers always contribute only negligibly to the surface tension. [3]

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The properties of fluid interfaces are often determined by the physics and chemistry happening right at the boundary between two components or two phases. The unavoidable presence of thermal capillary waves, however, contributes to smear any position-dependent quantity precisely on that length scale, where the fluid changes behavior from surface-like to bulk-like. Using computer simulations, it is possible to identify the molecules residing in the outermost layer (and in the following ones) in one of the two phases/components, and analyze the properties of the fluids either based on the local (intrinsic) distance from the interface, or on the liquid layer in which the molecules are residing. After a brief review of the computational methods developed to perform such analyses, I will present recent results on the interfacial properties of liquid/vapor interfaces, discussing among others: the location of surface tension in molecular liquids; two-dimensional hydrogen bond networking at the water surface ; the estimate of surface entropy; open problems in partially mixing systems and future technological developments.

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## Spontaneous electrification of fluoropolymer-water interfaces probed by electrowetting

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Fluoropolymers are widely used as coatings for their robustness, water-repellence, and chemical inertness. In contact with water, they are known to assume a negative surface charge, which is commonly attributed to adsorbed hydroxyl ions. Here, we demonstrate that a small fraction of these ions permanently sticks to surfaces of Teflon AF and Cytop, two of the most common fluoropolymer materials, upon prolonged exposure to water. Electrowetting measurements carried out after aging in water are used to quantify the density of ‘trapped’ charge. Values up to  $-0.07$  and  $-0.2 \text{ mC/m}^2$  are found for Teflon AF and for Cytop, respectively, at elevated pH [1]. A similar charge trapping process is also observed upon aging in various non-aqueous polar liquids and in humid air. A careful analysis highlights the complementary nature of electrowetting and streaming potential measurements in quantifying interfacial energy and charge density. We discuss possible mechanism of charge trapping and highlight the relevance of molecular scale processes for the long term stability and performance of fluoropolymer materials for applications in electrowetting and elsewhere.

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## Toroidal seeds for investigation of heterogeneous crystal nucleation of colloids

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Toroidal seeds are ideal to investigate the effect of curvature on heterogeneous crystal nucleation of colloids as a torus is positively curved on its outside and negatively curved on its inside. Due to surface tension toroidal droplets will either break[1,2] into single droplets via the Rayleigh Plateau instabilities and/or shrink[2] to a sphere unless there is an opposing force that stabilizes them. This can be done in a yield stress material[3].

Tori are made through the injection of a fluid into another immiscible material, while the two materials are in a relative rotational motion. The process of making a torus can be seen as a 3D printing process, where a needle's tip is printing into a suitable media. The outer continuous phase is chosen to be a yield stress material in order to stabilize the produced tori against the instabilities due to surface tension. Tori can be made in water and oil based yield stress materials. Tori out of NIPAM (N-Isopropylacrylamide) monomers are polymerized to produce stable toroidal hydrogels. Next the pNIPAM tori are transferred into a solvent in which colloidal particles can be studied.

Stable toroidal hydrogels of various sizes can be made using a 3D printer setup using an automatized stage (XPS Motion Controller and Linear Stages, Newport) and be used for heterogeneous nucleation studies using confocal microscopy. Having colloidal particles of  $\approx 2$  microns our aim is to make tori with characteristic radii of curvature of 25 to 50 microns.

At the conference I will highlight the steps that can be done to make tori that are small enough for microscopy experiments with colloidal particles. In addition I will show first microscopy images of colloids surrounded by these tori.

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Molecular diffusion in living cells has been found to deviate from free brownian motion [1]. Such diffusion is characterized by time-averaged mean squared displacement (MSD) with the anomalous diffusion exponent  $\alpha$  which distinguishes the sub- ( $0 < \alpha < 1$ ) and super- ( $\alpha > 1$ ) diffusion. Main factors of the anomalous diffusion are considered to be (i) macromolecular crowding and (ii) spatial confinement in micrometer space by the biological membrane [2,3]. Numbers of experimental reports in vivo and in vitro indicate that the crowding environment induces sub-diffusion ( $\alpha < 1$ ) [1]. On the other hand, the confinement effect has not been fully elucidated, despite its importance in various biochemical reactions and phase transitions [2,4,5]. In addition, the confinement in micro-metric space may vary the crowding effect depending on the spatial size. Therefore, we examined the correlation between the crowding effect and the confinement effect on the molecular diffusion systematically. We used water in oil (W/O) micro-droplet covered with a lipid layer of phosphocholine (PC) as a cell model [5] and the molecular diffusion inside of the droplet was monitored by fluorescent correlation spectroscopy (FCS). The droplet size is easy to control, which enabled us to study various size of confinement in the range of 10 – 200  $\mu\text{m}$  diameter. Enhanced green fluorescent protein (EGFP) and a linear polymer, polyethylene glycol (PEG) were used as diffusing molecule and crowder, respectively.

First, the autocorrelation functions (ACFs) were analyzed by a fit with Fickian model equation to deliver the diffusion constant  $D$  in the time scale of 0.05 - 32 ms. We found that the diffusion constant  $D$  increases as confinement size decreases when the PEG concentration is above the overlap concentration  $c^*$ . Secondly, we fit the ACFs with fractional Brownian motion (FBM) model equation [6] to extract characteristic relaxation time  $\tau_D$  and anomalous diffusion exponent  $\alpha$ . The  $\tau_D$  decreases as the confinement size becomes smaller. While the  $\alpha$  increases as the confinement size is smaller and reaches even  $\alpha > 1$ . Again, these result is observed only when the macromolecular concentration is above the overlap concentration  $c^*$ . The confinement effect on  $\alpha$  is in contrast with the crowding effect.

These experimental results indicate the strong interplay between the macromolecular crowding and spatial confinement on molecular diffusion. Furthermore, they may have antagonistic effect on anomalous exponent  $\alpha$ . Molecular diffusion in a cell is reported heterogeneous [7]. Hence, cells may regulate molecular diffusion through balancing between the crowding condition and the confinement size in order to optimize their metabolisms spatiotemporally.

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## Predictive modeling of molecular self-assembly at an electrochemical solid–liquid interface

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In recent experiments [1] the spontaneous and reversible transition between two- and three-dimensional self-assembly scenarios of a supramolecular system (PQPClO<sub>4</sub>) at a solid–liquid interface under electrochemical conditions [Au(111) in 0.1 M HClO<sub>4</sub>] has been shown. By a simple variation of the interfacial potential, it was possible to selectively organize the target molecules in an open porous pattern, to fill these pores to form an auto-host-guest structure or to stack the building blocks in a stratified bilayer.

In complementary theoretical investigations effort was dedicated to rationalize these experimental observations. To this end the molecules were modeled either as simple steric entities, endowed with multipolar moments, which reflect the actual charge distributions of the individual atoms that build up the molecule; alternatively, *ab initio* based interactions were included to complement the steric interparticle interactions. The self-assembly scenarios of these molecular models at the solid–liquid interface were studied and identified via optimization tools that are based on evolutionary algorithms. The complexity of the problem forces us to use advanced ideas of these optimization tools. Specifically, we employ a basin hopping based memetic search approach which combines heuristics, making use of already obtained knowledge, and deterministic local search strategies. The evolutionary operations as well as the local search strategies are optimized for the self-assembly problem such that the most favorable solutions in configuration space can be explored efficiently, gradually approaching the global optimum.

Our theoretical results allow to predict, on the basis of the underlying molecular model, the experimental conditions under which the various self-assembly scenarios can be observed. In addition, indications about the location of the ClO<sub>4</sub><sup>−</sup> anion relative to the cation can be given, an information which is not accessible experimentally.

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## Effects of water dissolution on the dispersion forces in nanosized alkane

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Van der Waals forces result from electrodynamic interactions between the bodies separated by a thin interlayer. They bear a universal character, acting between the bodies with any chemical nature and represent one of the strongest types of interactions at small separations. There are several approaches to calculate the van der Waals forces for one-component liquid films. However, the analysis of diluted solutions is poorly addressed. In our work, we have adopted a coupled fluctuating dipoles method based on a microscopic approach that accounts for many-body interactions to compute the van der Waals forces in wetting films of water solutions in alkanes. We have analyzed the peculiarities of the surface forces in films with thicknesses of a few molecular diameters, where the macroscopic theory is restricted in application. The problem addressed in our study is related to the influence of the dissolved water on the excess energy of the wetting film. It is shown that for small concentrations water molecules are preferably adsorbed on the alkane-air interface and thus for this system water acts as a surfactant.

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Thin films with complex architecture and controlled response to external stimuli are vital for designing responsive functional coatings. Polymers are widely used in such applications, however with the limited level of external control. A more responsive system would be composed of filaments where polymer linkers bind together colloidal beads that can be individually manipulated by external fields. Here we report on computer simulations of magneto-elastic filaments in external magnetic fields. The filaments are composed of superparamagnetic colloidal particles linked with flexible linkers. Upon being subjected to external magnetic fields, the filaments assemble into a rich variety of structures due to the competing elastic and induced magnetic interactions.

We study the phase behaviour of isolated filaments [1] that assemble into bent rods, hairpin-like structures, anchored sheets and collapsed structures – reminiscent of folding of proteins. We explore the phase behaviour of surface-anchored filaments composed of different sequences of magnetic and neutral colloids. In dense systems of surface-grafted filaments we observe exciting collective phenomena. We demonstrate how varying the external magnetic field can efficiently control the morphology of the coated surface [2].

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# Estimating Differential Capacitance of the Electric Double Layer in Ionic Liquids using Computer Simulations

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The electric double layer (EDL) is a region occurring at the interface between two phases, most commonly an electrode and an electrolyte. Differential capacitance occupies the central role in the theories of EDL. First of all, it is one of the few observables that can be directly compared to experimental measurements. Additionally, it describes the magnitude of electrolyte response to the change in applied potential. Finally, the differential capacitance is in the heart of modern technologies such as supercapacitors and batteries [1]. While the basic theory behind the interface between dilute electrolytes and electrodes has been established, the EDL occurring between metal surfaces and concentrated electrolytes, such as ionic liquids, represents a challenge for theory [2,3].

The present work focuses on the influence of the electrode nature and surface structure on the differential capacitance of ionic liquid. Specifically, we quantify the effect of 1) electrode quantum capacitance (see also [4]) and 2) surface charge distributions on the differential capacitance in 1-ethyl-3-methylimidazolium tetrafluoroborate. We demonstrate that in case of graphite electrode the shape of capacitance curve is largely determined by the electronic structure, which agrees with previous experimental results [5]. A more detailed analysis provides insights towards potentially useful combinations of electrode and electrolyte, capable of yielding significantly higher capacitances that are required for advanced electrochemical devices.

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## Evaporation and Boiling in Thin Gap

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Laminated steel plates are widely used as metal cores in various types of electric transformers. These cores are often immersed in insulating mineral oils, and it requires time and cost to wash the oil away when disposed. The main target of this study is the cleansing process of such laminated plates. Recently a method of vapor washing with organic solvents has been proposed [1]; it is experimentally confirmed that, under sufficiently high temperature (typically 100~200 °C, depending on the solvents) and low pressure conditions, the mineral oil between the core plates is gradually replaced by the solvent vapor and completely washed away. To understand the washing mechanism and optimize the process, it is essential to investigate the phase change dynamics in such narrow gaps in more details.

To study the washing mechanism of laminated plates with solvent vapor, we have experimentally investigated evaporation dynamics of liquid confined between solid plates under reduced pressure [2,3]. As the test liquid, we use deionized water and several organic compounds (e.g., ethanol, acetone, heptane). Most of the experiments were done at room temperature under reduced pressure (typically 1-10 kPa). To visualize the fluid motion in the thin gaps, we adopt glass plates. When a test liquid is sandwiched between a normal (float) glass plate and a ground (sand-blasted) one of surface roughness ~30 μm, vertically incident light passes through the plates without much scattering; once the liquid starts to evaporate, dried rough surface of the ground glass scatters the light and we can monitor the flow pattern.

Based on the transmitted light intensity, the whole plate area is categorized into three regions; completely wet, completely dry, and semi-dry one; the last one is supposed to be the state that thin liquid film spreads on the plate. In the case of water, many tiny spots of semi-dry region appear and expand at the initial stage, which is probably cavitation of dissolved gas. In organic liquid cases, evaporation seems to start from the edges of the plates. At a later stage, the semi-dry region expands with complicated branching patterns. In all cases, occasional rapid motions of liquid were observed, which correspond to two dimensional flash boiling. The influence of the control pressure, the surface roughness, the plate temperature, and the plate deformation were also investigated.

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## Coarse-grained molecular simulations for semi-flexible polyelectrolyte brush

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Ionic interactions in solid-liquid interface plays important role since the long range Coulomb interaction is the essentially the most strong intermolecular interaction. Polymers are used in electrodes of secondary batteries, as binder of carbon based active materials. In case the polymers are charged and stiff, the cycle performance is improved than other polymers [1]. In order to examine the role of the charge, we used metropolis Monte Carlo Brownian Dynamics simulations [2] for semi-flexible polyelectrolyte brushes with counter-, and co-ions to study the sturcture and dynamics of ion environment [3]. We found that the counterion condensation is found when the linear charge density is above the critical value. Moreover, the ion transportation under the external electric field is enhanced due to the condensation.

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## Dynamics of a colloidal Particle near a Gas-Liquid Interface

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The physical behavior of colloids suspended in a fluid close to a solid wall has been well characterized in the past [1]. Conversely the dynamical behavior of a particle close to a fluid interface is a relatively new field with strong implications in green and food processing [2]. Previous focus was limited to spherical particle's viscous drag close to the interface [3] and wetting dynamics after interface breaching [4].

In this paper we present experimental results on the dynamics of micrometric colloids (spheres and ellipsoids) close to an interface between water based solution and air prior to the particle's interface breaching.

In order to study such dynamics we use a home-made pending-drop setup where particles dispersed in water based solutions (mixture with heavy water and/or with salt at different molarity) sediment towards the interface with air of the drop. The drop curvature is adjusted via the water solution pressure in order to obtain a flat interface at the particle scale. All the particle's degrees of freedom (i.e. distance from the interface, position in a plane parallel to the interface and, for ellipsoids, orientation) are measured tracking the particle-interface interference patterns using incoherent leds with three different wavelengths.

The typical dynamics of a particle approaching the interface shows an initial sedimentation regime driven by gravity and viscous drag. Closer to the interface a second regime arises which strongly depend on the solution molarity and density and particle morphology. For both particles morphologies the sedimentation dynamics stops at a distance from the interface of the order of hundreds nanometers. At small molarity (0.5 mM) both type of particles fluctuate around this position during the entire experimental observation time interval ( $10^3$  s). Increasing the molarity, ellipsoids more easily than spheres start to escape from this position approaching rapidly the interface till a distance of few nanometers. Such observations point out the importance of the electrostatic and morphology in the interaction with the interface. A calibration of this interaction will be presented by taking advantage of the buoyancy driving force changing the solution density.

Building up on all these experimental observations, a model considering the interplay between all the contributing interactions (i.e. gravity with buoyancy, electrostatics and Van der Waals) will be discussed and compared to the experimental results.

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## T-ramp tracking of colloids with controlled adsorption on flat substrate

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Colloids with adhesion properties reversibly tuneable by shift of pH, T, light etc. can be designed using coatings with stimuli-responsive polymer chains. The aim of this work is to decipher **transient dynamic** of these colloids in presence of flat substrate.

In order to have reversible and T-controlled interactions, silica beads were coated by mixed solutions of poly(lysine)-grafted-polyethylenoxide (PLL-g-PEG, for steric repulsion) and PLL-g-PNIPAM (i.e. PLL with poly-N-isopropylacrylamide temperature-responsive side chains). PEG-coated particles were stable in suspension in the whole experimental temperature window, while the presence of PNIPAM in the particle's corona provided, at  $T > 32 \pm 1^\circ\text{C}$ , reversible adsorption on flat substrate. Real-time 3D tracking method was used to monitor (x,y,z) positions of particles in suspension above microscope glass slides during the T-triggered adsorption transition and varying the surface molar fraction,  $f$ , of PLL-PNIPAM.

*Ascending T-ramp* was applied with rate  $r[^\circ\text{C}/\text{min}]$ , between  $28^\circ\text{C}$  and  $38^\circ\text{C}$ . Particles in brownian motion get progressively adsorbed on the surface. The brownian dynamics immediately before sticking and the adsorption rate depend on molar fraction  $f$ . Repeating ramps with different rates  $r$  reveal time scales of polymer shield breakdown as function of  $f$ .

*Descending T-ramp.* Starting from high T, when all particles are adsorbed, decrease of the temperature desorbed gradually all particles. The brownian motion immediately after desorption was monitored and analyzed. The diffusion constant and the desorption rate are this time independent on  $f$ .

*Confined particle motion.* Adsorbed particles are not immobile: their dynamics corresponds to a brownian motion in confining potential. The strength of the confinement, as extracted from data fitted to Langevin equation solution, is an increasing function of  $f$ .

The resulting tracking records were analyzed and compared to theoretical results calculated using Smoluchowski-Fokker-Planck equation for sedimentation problem with partially reflecting boundary conditions and near-wall diffusion hindrance due to hydrodynamic interactions.

We believe that present findings on transient dynamics of T-triggered adsorption-desorption of colloids can contribute to the efforts for design of new separation techniques based on time-modulated external stimuli.

## Crowdedness of fluids in confinement

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Although many investigations have been devoted to the study of fluids confined in random porous media since 1988 when Madden and Glandt proposed the first theoretical quench-annealed mixture model for fluids confined in random porous media [1-16], no precise measure has ever been proposed to describe quantitatively the quench effect for the adsorption of a fluid in a random porous material. Here, we suggest to measure such a confinement effect by calculating the difference of free energy for inserting a fluid particle into a quench-annealed system or into an equilibrium binary mixture with the help of both Monte Carlo simulation and scaled particle theory (SPT). Although it appears to be a common sense to measure the crowdedness of a fluid system by the densities of the species constituting it, we show that this ceases to be valid for confined fluids under some conditions. A quite thorough investigation reveals that when the size of fluid particles is larger than that of matrix particles, the quench-annealed system can appear much more crowded than its corresponding equilibrium binary mixture, i.e., having a much higher fluid chemical potential, even when the density of each species is strictly the same in both systems respectively. We believe that the insight gained from this study should be useful for the design of functionalized porous materials, e.g., for high-capacity gas adsorbents etc.

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## Co-assembly of amphiphilic Janus disks and small molecules in two-dimensional systems

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In recent years, there is an increasing interest in the design and synthesis of Janus particles and their self-organization. The theoretical modelling of the self-assembly is a difficult task. Nevertheless, this process has been intensively studied using different theoretical approaches and computer simulations [1,2].

In this contribution we study the self-assembly in a mixture of amphiphilic Janus particles and isotropic molecules using Monte Carlo method. Our aim is to show a role of the fluid molecules in the process of self-organization. In our model each Janus disks consists of two semicircles, one being attractive (*A*), while the other one is repulsive (*R*). The fluid molecules are attracted by the *R*-patches of Janus particles and repelled by the *A*-patches. Interactions between particles are modelled using the potential proposed in earlier works [5, 6].

We show that the amphiphilic Janus disks and small fluid molecules assembly into different mixed structures at temperatures when the both components are supercritical fluids, if considered separately. The structure of the system depends strongly on a fluid density. The addition of a trace amount of fluid molecules to Janus particles leads to the formation of a highly ordered, solid-like structure. At moderate densities, fluid molecules are encapsulated between long strings of Janus particles. Such "mixed wires" form a gel-like phase for moderate densities of Janus particle. In the case of high fluid densities Janus particles aggregate in finite clusters. The evolution of the system structure is continuous. The self-organization follows from anisotropic interactions between particles. "Adsorption" of fluid molecules on repulsive parts of Janus particles plays a key role in the process.

The bond-switching between Janus particles is observed as the fluid density varies. The *AA*-bonds between Janus particles are energetically preferred. However, fluid molecules can act as linkers between Janus particles leading to *RFR*-bonded clusters. For extremely low fluid densities there are almost the same numbers of *AA* and *RFR*-bonds. On the contrary, for moderate fluid densities the *RFR*-bonds are more probable. In dense fluids Janus particles are always joined by *A*-patches. The similar bond switching caused by changes in temperature was observed in experiments.[5]

The study can provide a guide for the design of novel superstructures via co-assembly of Janus particles and fluid molecules.

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# Field-driven population inversion in a confined colloidal mixture: following the time evolution by Langevin dynamics simulation.

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The influence of an external field on the composition of a binary colloidal mixture confined in a finite-length channel is investigated by simulation. The transition from a near-bulk composition to an inverted population[1] is studied as a function of time using Langevin dynamics simulations[2]. For state points corresponding to reversible field cycles, the cyclic filling and emptying of the channel by the dipolar minority species are compared. A series of simulations at increasing value of the damping parameter are performed in order to extrapolate the physical relaxation times to the colloidal regime. We also discuss the scaling with the particles size of the characteristic cycling time of reversible field cycles. For state points at which the mixture is unstable at zero field, reproducible irreversible cycles are illustrated.

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## Explaining the Cassie–Wenzel transition with X-ray microscopy

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A water droplet on a microtextured hydrophobic surface usually exhibit distinct two wetting states: the Cassie-Baxter state in which air is confined between the droplet and the surface or the Wenzel state in which the droplet completely penetrates through the surface [1]. Understanding the wetting transition from the Cassie-Baxter to the Wenzel states is important to design stable hydrophobic surface without breaking down [2]. Despite decades of experimental and theoretical studies, interfacial energy barrier of penetrating liquid meniscus is not well estimated because of limited penetration capability of optical techniques for directly visualizing the transition. Here we study the transition from the Cassie-Baxter to the Wenzel states by utilizing high-resolution high-penetration X-ray microscopy. The curvature evolution of the meniscus is demonstrated by direct visualization of penetrating water meniscus during intermediate states of the transition. We believe that X-ray microscopy would be a powerful tool to reveal the dynamics of liquid penetration into a microtextured superhydrophobic surface.

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## Three-dimensional force balance of asymmetric droplets

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A horizontal force balance among vapor, liquid, and solid determines an equilibrium contact angle of a droplet: this balance is known as Young's law. In fact, the classic wetting law is valid only for axis-symmetric droplets such as spherical sessile droplets. However, actual droplets can often exist as asymmetric droplets: for instance, a droplet on a thin membrane film [1, 2]. It is difficult to directly and precisely observe the contact line of an asymmetric droplet using conventional optical imaging techniques. Here we show a useful approach with X-ray microscopy. Thanks to the small wavelengths of hard x-rays, x-ray imaging can offer high spatial and temporal resolutions. The microscopic observation with X-ray microscopy shows that three-dimensional force balance should be considered to explain the wetting behavior for an asymmetric droplet. By visualizing an asymmetric droplet placed on a free-standing membrane in air, we are able to identify that the unbalanced surface energy along the contact line determines pinning behaviors during evaporation of the droplet. We believe that X-ray microscopy is powerful for evaluating the three-dimensional force balance, which would be important in a variety of actual wetting situations.

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## Nano-Mechanics with the force feedback microscope: from capillary bridge dynamics to noncontact indentation

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The atomic force microscope (AFM), has a unique capacity for measuring forces at the nanoscale. However, a sensitive AFM cantilever will “jump-to-contact” upon nucleation of a water nanobridge, which makes its study difficult. The force feedback microscope (FFM) uses interferometric detection to measure the motion of the AFM tip while using a feedback loop to maintain the average tip position constant [1]. With this strategy it is possible to avoid the tip “jump-to-contact” even if a water bridge forms between the tip and the substrate. Using this unique setup, we have explored the dynamics of water nanobridges from hundreds of Hertz to hundreds of kHz and have identified a transition characterized by a fast stiffening of the water bridge as frequency is increased.

Another application of the FFM relates to the measurement of the nano-mechanical properties of an object. In conventional indentation experiments involving contact, among other difficulties, one needs to cope with adhesion which often complicates experiment and model. Using a surface force apparatus Leroy et al [2] demonstrated that a fluid can be used as an intermediary between the tip and the sample, allowing for the determination of the mechanical properties of a sample while avoiding direct contact. The same strategy has been successfully implemented with an FFM.

In this talk I will briefly introduce the FFM strategy and discuss these two key results, capillary bridge dynamics and noncontact indentation.

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## Drop impacts onto mobile and fixed particles rafts

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We experimentally probe the ability of hydrophobic particle assemblies to efficiently prevent the interface they lay on from coalescing with drops that impact onto them. Two kinds of assemblies are considered: for mobile rafts, the particles are attached to the air/water interface by capillary forces and can move along the surface, while for the immobilized rafts, the particles are fixed in an aqueous agarose gel and can not move. In both cases, the particles form a monolayer which surface density is adjusted to the one of the monolayer collapse threshold [1]. Particles of 110 $\mu$ m and 190 $\mu$ m diameter are used either separately or in mixtures varying the surface fraction of small particles. When water drops impact onto these assemblies, two outcomes are possible: either the water of the drop comes into contact with the water or the agarose gel on which the particles are adsorbed, we refer to this as to a “coalescence” event or it remains isolated by the particles corresponding to a “non-coalescence” event.

For both kinds of assemblies and a given drop size, the monodisperse rafts show sharp transitions between coalescence and non-coalescence which can be well described by threshold velocities. For mobile particles, the raft is distorted upon impact creating a “hole” free of particles which leads to coalescence when reaching a critical size. The hole critical size is given by the ability of the particles, present at its periphery, to prevent the drop and the puddle interfaces to touch each other [2]. In brief, the larger the particles, the better the protection. An opposite effect is observed onto immobilized rafts. There, the drop interface has to progress through the fixed monolayer. As for any porous media, the smaller the pores (and therefore the particles), the stronger the pressure loss and thus, the greater the velocity threshold.

In contrast to other mechanical forcings such as compression or bending [3-4], no collective effects can be observed in the bidisperse mixtures and sharp velocity thresholds are replaced by the coexistence of both coalescence and non-coalescence events for velocities ranging between the monodisperse thresholds. Indeed, the coalescence mechanism is very local for both kinds of assemblies. For mobile rafts, the distribution of the particles around the “hole” is relevant while the pore size distribution is critical for immobilized rafts. We show that an approach based on the probability to find small (or large) particle enclave may be used to estimate the probability of coalescence for mobile (or immobile) rafts.

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## Study of intercalation complexes of kaolinite with primary intercalation reagents

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Delamination/exfoliation of platy kaolinite (a common representative of the two-sheet type clay minerals) has been found to be one of the most favorable ways to produce aluminosilicate nanoscrolls. For the delamination of the kaolinite layers, multi-step intercalation/deintercalation procedures are used. In the first, direct intercalation step, the intercalation reagents are typically small organic molecules possessing high dipole moment. We modeled the incorporation of formamide, urea, N-methylformamide and dimethyl sulfoxide molecules into the interlayer space of kaolinite by classical molecular simulations. Realistic CHARMM-based atomic force fields were applied in detailed molecular dynamic simulations using the GROMACS software package. Besides the determination of characteristic basal spacings of the intercalation complexes, we compared the density and orientation distributions of the guest molecules. From the trajectory frames of the simulations we also calculated the typical intermolecular interaction energies. It was found that the guest molecules have profoundly stronger interactions with the octahedral surface.

## Using nanopores as sensors: a Monte Carlo modeling study

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We can distinguish natural (e.g., ion channels) and synthetic nanopores (e.g., carbon nanotubes, nanopores etched into plastic foils). The length of synthetic nanopores belongs to micrometer, while their radius belongs to the nanometer length scale. Ion transport through the nanopore has two main properties: rectification and selectivity. Due to these properties, the nanopore can be used as a rectifier diode or as a sensor. In this work, I examine the applicability of a nanopore as a sensor. We located binding sites inside the pore which are selective for the analyte, that is the molecule to be detected in the electrolyte filling the pore. Binding these particles to the nanopore's walls reduces the effective cross section of the nanopore, and, consequently, reduces the current carried by the main ions of the electrolyte through the pore. By measuring the drop of the current and constructing calibration curves, we can determine the concentration of the analyte.

In this modeling work, we create simple models the membrane, the pore, and the electrolyte. Negative charges are located on the cylindrical pore's wall to make the pore cation selective. For the electrolyte, the Primitive Model of electrolytes is used, which treats the ions as hard spheres with their charges located in the centers, and the solvent (water in this case) as a constant dielectric continuum. The binding sites are modeled with a square-well potential. The system is examined with the Local Equilibrium Monte Carlo (LEMC) method which is applicable for non-equilibrium systems. The currents of ions were calculated with the Nernst-Planck (NP) equation. This model and the method [1] (NP+LEMC) is suitable for examining low concentrations, that is important because the analyte is usually present in very small concentrations.

We examine the effect of various model parameters (for example, number, strength, and width of the binding sites; properties of the electrolyte and the analyte) on the sensitivity of the sensor by preparing calibration curves with different values of these parameters. Through the calculated concentration and potential profiles, the molecular mechanisms of the system can be observed well.

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## Multiscale modeling of rectifying bipolar nanopore: explicit-water versus implicit-water simulations

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Multiscale modelling is getting more and more important as our devices are getting smaller and smaller. Nanopores in nanofluidic devices can function as the central working units and the behaviour of selectivity and rectification can be determined here also.

Here we present computer simulation results for a rectifying bipolar nanopore on two modeling levels. In an all-atom model, we use explicit water to simulate ion transport directly with the Molecular Dynamics technique. In a reduced model, we use implicit water model and apply the Local Equilibrium Monte Carlo method together with the Nernst-Planck transport equation. This hybrid method makes the fast calculation of ion transport possible at the price of lost details. We show that the implicit-water model is an appropriate representation of the explicit-water model when we look at the system at the device (i.e., input vs. output) level.

We find profound differences between the two models looking at details of concentration and potential profiles that do not influence the basic behavior of the model as a device

Our simulations show that reduced models can still capture the overall device physics correctly, even though they get some important aspects of the molecular-scale physics quite wrong; reduced models work because they include the physics that is necessary from the point of view of device function. Therefore, reduced models can suffice for general device understanding and device design, but more detailed models might be needed for molecular level understanding.

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## Droplets, capillary interactions and self-assembly from the equilibrium shape of fluid-fluid interfaces

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By using a recently-introduced numerical method based on a Monte Carlo approach[1], we are able to compute the equilibrium shape of fluid-fluid interfaces in contact with given solid surfaces, possibly curved and possibly with chemical heterogeneities.

Here we present an overview of our results for colloidal particles adsorbed at fluid-fluid interfaces [2,3], droplets wetting rod-like particles with asymmetric shape and different aspect ratios [4], and droplets wetting solid flat substrates with ellipsoidal patches of enhanced lyophilicity [5].

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## Magnetically tunable wettability of soft magnetoactive elastomers

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Dynamically responsive surfaces receive increasing attention in different areas of modern technology. Touch-based interface systems and devices are well known examples. Magneto-active elastomers (MAEs) belong to materials with promising properties for this group of applications [1]. These composite materials comprise micrometer-sized ferromagnetic particles dispersed in a non-magnetic elastomer matrix. Some recently developed MAEs with highly compliant elastomer matrices display very large (over several orders of magnitude) magnetic-field induced changes of dynamic elastic moduli [2]. These materials were also found to be promising as magnetically tunable platforms for some non-conventional applications, such as biological cell cultures [3]. As cell growth takes place on the surface of substrates, it consequently depends on the substrate's surface properties and its topography.

In this contribution, we report a systematic investigation of surface morphology of soft MAEs as a function of the applied external magnetic field. The samples contained 70 wt% of carbonyl iron powder embedded into a soft PDMS matrix. Their properties were analyzed as a function of magnetic flux density  $B$  in the range between 0 and 250 mT. The investigation methods included optical microscopy, optical profilometry and diffuse optical reflectance measurements. The results showed that surface roughness strongly depend on the applied magnetic field. In the absence of magnetic field, the RMS roughness is considerably below 1 micrometer, while for  $B=250$  mT it increases to a few micrometers. Considerable hysteresis of optical surface properties is observed for increasing or decreasing magnetic fields. We also investigated the contact angle of water droplets deposited on the surface of MAE films. It was found that the value of the contact angle, which is around 100 deg, can be rapidly decreased (response time is below 5 s) by approximately 10 degrees if the external magnetic field is increased from 50 to 200 mT. Within the accuracy of measurement, this change is reversible.

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## Melting scenarios and unusual crystal structures in two-dimensional core-softened potential systems

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Recently, there has been growing interest to investigation of behavior of confined fluids, with a special attention to the water. Water plays an important role in many natural processes where it is confined or at contact with substrates, for example, in rocks, in biological cells, at contact with surfaces of proteins, in biological membranes, etc. It is well known, that the qualitative behavior of water, including the water-like anomalies, can be described using the core-softened potentials with two length scales.

In the talk we present the computer simulation study of phase diagram of a two-dimensional system with core-softened potential. It is shown, that in the contrast to the case of simple potentials, like soft disks, where the ground state always corresponds to the hexagonal close-packed structure, the various structure are possible including the square lattices recently found in experiments. The possible melting scenarios are discussed and the deviations from the widely accepted Berezinskii-Kosterlitz-Thouless-Halperin-Nelson-Young (BKTHNY) scenario are discussed [3-6]. The influence of the random disorder, which is inevitable in real experiments, on the melting scenario is considered. It is found that depending on the form of the potential, the melting of the system occurs through one first order transition or through two-stage transition with continuous BKT type solid-hexatic transition and first order hexatic-liquid transition. Random pinning transforms the first order transition into two-stage melting scenario or widens the hexatic phase [5,6]. It gives the possibility to study the behavior of the diffusivity and order parameters in the vicinity of the melting transition and inside the hexatic phase.

We expect that such a phenomenology can be checked in confined monolayers of charge-stabilized colloids with a softened core and water confined between two hydrophobic plates.

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## Structural forces acting between negatively charged surfaces in micellar solutions studied by CP-AFM

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Structural forces in complex fluids can arise when high concentrations of objects, such as polymers, polyelectrolytes, nanoparticles or micelles are confined between two surfaces. With approaching surfaces, layers of particles get squeezed out resulting in alternating osmotic pressure and therefore alternating attraction and repulsion. Interactions between the surfaces cannot only be described by the classical DLVO theory and has to be modified by the so called structural force. These forces have a similar origin as the well-known depletion force. After the pioneering theoretical description of depletion forces by Asakura and Oosawa, [1] the group of Israelachvili was the first to detect those structural forces experimentally by means of the surface apparatus technique. [2]

For a wide range of systems, oscillatory structural forces could be rationalized by a simple damped oscillatory profile. The wavelength  $\lambda$  is dependent on the nature of the particles. Uncharged particles could be described by a hard-sphere model and  $\lambda$  in the force profile represents the diameter of the depletants. Charged particles, however, repel each other. Because of that, the wavelength of the force oscillation scales with the number concentration  $c$  of the depletants, typically with  $c^{-1/3}$ . [3]

Although a theoretical description of the hard-sphere model for uncharged particles is established, the transition-point to the repulsive model for charged particles is still missing. We will present an insight into our experimental work visualizing the interactions between a silicon surface and a silica colloidal particle using Colloidal probe atomic force microscopy (CP-AFM). Micellar solutions of the non-ionic surfactants Brij L23 or Tween 20 were mixed with the ionic surfactant sodium dodecylsulfate (SDS) in different ratios. Oscillatory structural forces between negatively charged surfaces could be manipulated in that way.

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## Leidenfrost effect dynamics with conical surfaces

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The Leidenfrost state is typically studied by placing droplets on flat or slightly curved surfaces [1, 2]. Here this phenomenon is investigated by depositing water in hot conical bowls. We found that this phase exists even for large amounts of liquid (pure water, alcohol and acetone) in very narrow cones without considerable effect of the confinement on the Leidenfrost transition temperature  $T_L$ . Different chimney regimes and oscillation patterns were observed and summarized in a phase diagram [3]. As well, we present a theoretical model for heat transfer in a Leidenfrost drop.

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It is well known that Hertzian spheres system which belongs to the class of bounded potentials gives rise to a phase diagram with multiple re-entrant melting transitions in a wide range of densities [1]. Diffusion coefficient of the re-entrant fluid shows unusual nonmonotonic curves with increasing density like the ones observed in water [1, 2]. This rich behavior together with the simplicity of the potential functional form makes the Hertz model an attractive one for the study of supercooled dynamics.

We perform molecular dynamics simulations of the Hertzian disks system consisted of 20000–22500 particles. We use equations of state, behavior of the orientational and translational order parameters, as well as their correlation functions for the calculation of the lines of phase transitions between different phases observed in the system. The dependence of the phase diagrams and the melting scenario on the parameters of the potential and the strength of the quenched disorder are investigated. The phase diagrams are discussed in a critical comparison of the results obtained in [3]. In the system with pinning a significant widening of the hexatic phase was observed in comparison with [4]. Particular attention is paid to the influence of random pinning on the transition scenario between crystals with six-fold hexagonal and four-fold square symmetries and the diffusion coefficient of the re-entrant hexatic and tetratic fluids at low temperature.

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## Selectivity of large hard sphere on a hard wall immersed in binary hard-sphere fluid

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Adsorption phenomenon in a solution phase are industrially important such as separation and purification of certain molecules from the solution. The affinity between surface and the molecule has been often discussed based on the direct attraction. However, it is not trivial. D. Chandler, et al. published a series of study for van der Waals picture of the liquid structure  $g(r)$ . According to the van der Waals picture, *“the average relative arrangements and motions of molecules in a liquid (that is, the intermolecular structure and correlations) are determined primarily by the local packing and steric effects produced by the short-ranged repulsive intermolecular forces”* [1]. Here, we examine the selectivity of molecules based on the short-ranged repulsive intermolecular forces.

A model hard wall, huge hard sphere, is immersed in a binary hard sphere fluid. The spatial distribution functions between the wall and the particle in the binary fluid are calculated by using an integral equation theory of liquid, HNC-OZ theory. The amounts near the surface are obtained from the distribution functions. We also obtained the potentials of mean force between the wall and the particle, and the activation free energies from the bulk to the surface are estimated. Mole-fraction of these values are obtained and plotted. The packing fraction is kept in the calculation of mole-fraction dependence.

The results show that the wall selects larger hard spheres from the binary fluid. The selectivity becomes larger as the size ratio increases. In case of the size ratio 2.0, even in the mole fraction is 0.5, the amount of adsorbed larger hard sphere at the mole fraction 1.0 is almost maintained. This behavior becomes strong as the size ratio increases. The calculated activation free energies also show interesting results. The activation free energies for one component fluid are larger than that for mixture. Above behaviors are also observed in experiments for absorption behavior of inert porous material in inert binary solvent. We will discuss above behaviors and validity of the van der Waals picture in these phenomena.

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## Application of design of experiments to coarse-grained molecular dynamics simulations: wettability of liquid resins

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Resin materials are widely used for various industrial purposes such as insulation, coating, and adhesive materials. In manufacturing processes, resin materials are synthesized in a liquid state and mainly consist of small molecules like monomers. Industrially, the wettability of liquid resin materials is important because it affects the synthesis and later curing processes. Therefore, wetting behaviors of monomer resin molecules should be revealed in detail. In particular, wetting behaviors are closely related to resin structures. Thus, their relationship must be elucidated. To investigate resin materials, coarse-grained molecular dynamics (CGMD) simulations are fruitful [1]. This is because a CGMD simulation has a low calculation cost even though it can consider atomic level resin structures. However, applying CGMD simulations to various products requires huge computational resources and research time. To effectively use CGMD simulations, we focus on the design of experiment (DOE) [2]. The DOE is useful for designing tasks to evaluate properties with a small number of trials. Therefore, it is frequently used in industrial research such as mechanical properties. However, to the best of our knowledge, the DOE approach has not been applied to CGMD simulation studies. In this study, to elucidate the wettability of liquid resin materials and improve the usage of CGMD, we performed CGMD wettability simulations by using a calculation plan on the basis of the DOE.

The CGMD simulations are based on the bead-spring model [3]. In this study, three types of beads are used. A resin model is created by two types of beads. Four beads are put in a line in a resin model, and the two center beads and the two terminal beads are different types. A substrate model is created by one type of beads. To unravel the effect of resin structures on the wettability, the interaction energy of each pair of beads is changed. Thus, many simulation runs are essential more than 240 in our case. We reduced them to 18 by using an L18 orthogonal array created by the DOE approach. In the simulations, agglutinated resin models are put on the substrate model. Resin molecules spread along the substrate. After that, contact angles were calculated. The results of the 18 simulations indicated that the interaction energy between resin and substrate beads affects the contact angles and equilibrium time. Moreover, the resin center and terminal beads affects contact angles differently. This means the structure design of resin materials is important for wettability control. Finally, we conclude that the DOE approach is effective for the CGMD simulations and sufficient to elucidate the wettability of liquid resin.

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## Experimental studies on the detachment of multi-walled carbon nanotubes by a mobile liquid interface

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Retention and detachment of colloidal particles from surfaces is often considered only in terms of spontaneous chemical dispersion when the surface is already fully submerged. Nevertheless, interfacial processes, where the particles are abducted on a mobile liquid contact line by capillary effects are ubiquitous [1]. Theoretical description of such interfacial processes exist for spherical microcolloids, while for anisotropic shapes the literature is limited. The multiwall carbon nanotube (MWNT), especially when it is of a high quality, is an ideal anisotropic object to study experimentally these effects.

We present experiments in which a water-air-solid contact line is swept over a deposition of MWNT material on a hydrophilic substrate, causing selective detachment of irregular amorphous carbon particles (ACP) over the one dimensional MWNTs. The experiments are realized in different ways, either with droplets on a piece of Silicon wafer [2] or by immersion of the whole Si piece into water [3].

We investigate the detachment process and the balance between the surface tension force and adhesive forces, including the van der Waals force, the electrostatic double layer interaction, and the hydrophobic interaction [4]. The extremely different geometrical factors of the ACPs and the MWNTs leads to the selectivity of their detachment.

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# The study on the confinement effect of self-assembly process and structure in surfactant solution using coarse-grained molecular simulation

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For the past several decades, the self-assembly and the process of amphiphilic molecules have been significantly studied. Amphiphilic molecules in water solution exhibit characteristic structures depending on temperature, molecular structure, and concentration, and so on. It is important to control and predict self-assembly structure in the engineering field.

On the other hand, it is also known that fluids confined to nanoscale channels can exhibit new phases not seen in the bulk. In the previous paper<sup>[1]</sup>, we have performed a dissipative particle dynamics (DPD) simulations of self-assembling short-chain surfactant inside different nanotubes. Morphologies and polymorphic transitions are showed as the chemical characteristics of the inner surface of nanotubes are changed. Li *et al.* showed that self-assembled structures of amphiphilic molecules are changed by their hydrophobic property when they are confined in a vesicle<sup>[2]</sup>.

However, the foundational knowledge on self-assembly of amphiphilic molecules is not completely understood. In this study, we focused on difference of dimensional confinement and temperature, and investigated the detail of molecular self-assembly using a coarse-grained molecular simulation.

We used DPD method to investigate a self-assembly structure and process for amphiphilic molecules. The primitive equation is nearly Langevin equation. We examined three kinds of dimensional confined system, including a vesicle (0D), a nanotube (1D), and nanoslit (2D), and also investigated their self-assembly structures and processes. Each conditions has a characteristic length, it is a diameter or width: 30.0. Total number of particles is 70,685, number density is 5.0, and concentration is 10.5%.

We compared between each condition in mean aggregation number and temperature. Highest mean aggregation number was nearly the same in each condition. The difference is the temperature when appeared highest mean aggregation number.

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## Cavitation within a liquid micro-confined by a porous hydrogel

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Among numerous fascinating features, water can sustain high negative pressure and eventually relax its metastable state by nucleation of vapor cavities, a process named cavitation.

This study concerns experimental and numerical investigation of cavitation bubbles growth in a liquid micro-confined in a porous material. The system is inspired by the fern sporangium that exploits negative pressure and bubble cavitation to activate an ultra-fast movement and eject spores as a catapult [1] [2]. Encapsulating a micrometric volume of water in by a porous hydrophilic material -i.e. methacrylate hydrogel- is a easy way to mimick the natural system capturing its main features: water loss, liquid tension generation and bubble nucleation [3]. We developed a unique technique to perform simultaneously fast-imaging and acoustic measurements. It has recently been proved indeed that bubbles -nucleated in a confined system- oscillates before reaching an equilibrium volume [4], resulting in ultrasound emissions. For each bubble appearance, a pressure wave was detected with high-precision by the means of a needle hydrophone. Frequency and attenuation time of the pressure waves were characterized as a function of the confinement volume, finding perfect agreement with the theoretical model developed by O.Vincent et al. Moreover, numerical simulations were carried out to support our measurements and extend the range of investigation to smaller scales. The problem is addressed by means of a diffuse-interface formulation [5]: it enables the complete description of a complex vapor-liquid system and embeds surface tension, phase change and acoustic effects. With such a model, we were able to study bubble oscillations, acoustic emissions and their dissipation. Finally, we made a reliable comparison with experimental results thanks to a modified equation of state that perfectly describes water behavior in both vapor and liquid phase.

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## Contact angle of spheres floating at air-water interfaces by solving the Young-Laplace equation

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The wettability of any material is determined by the contact angle, which reflects the kind of interaction between the liquid and the material and, consequently, it has a deep relationship with the nanostructure of the material's surface. Hence, materials can be from hydrophilic to superhydrophobic depending on their surface chemical composition and geometry.

Imaging techniques are typically used to measure contact angles on flat surfaces. However, many materials with interesting wetting properties usually appear in non flat shapes. Small quasi-spherical particles are particularly common and measuring their contact angle by means of floatation has been already proposed [1-4]. However, this technique presents two main problems: i) the air-water interface is intrinsically three-dimensional due to the formation of a meniscus in the vicinity of the sphere, and ii) the precision of these measurements decreases with the size of the sphere as the relative dimension of the meniscus becomes greater.

In this work, we explore the possibility of using the contact angle to determine the kind of nanostructured material covering the surface. In order to avoid the above-mentioned technical problems, the protruded height above the air-water interface of a floating sphere is proposed as an indirect way to determine the contact angle, provided that the density contrast and the radius of the particle are known. Following previous theoretical and experimental works on floating spheres [1-4], we solve the Young-Laplace equation to simulate the equilibrium conditions of a sphere and the deformed fluid interface. We show that using this method, we can get the contact angle by the measurement of the proposed height and, consequently, one could obtain information about the properties of the material composing the spheres.

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## Hydration forces in water nanofilms confined between calcium carbonate surfaces

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Calcium carbonates are minerals with polymorphic properties, abundant in the earth's crust. They are the main building block of bones, shells, corals and similar man-made cementing materials such as industrial cement used world wide in construction work. Solvation forces is believed to play an important role in the calcium carbonate growth and dissolution process [1,2,3,4]. Solvation forces, or hydration forces when water is the solvent, arise from the structuring of water molecules confined between two surfaces at nanometer separation [5]. The ordering of the molecules is expected to vary with the structure of the surface and its hydrophobic character [5]. A better understanding of solvation forces is essential for developing new models of microscopic mechanisms explaining growth and dissolution initiated at the atomic scale, a key to improve mechanical properties of man-made cementing materials and to understand biomineralization [1,3,4].

In this study, grand canonical molecular dynamics simulations of water nanofilms confined between the calcium carbonate polymorphs, calcite and aragonite, has been performed. The adsorption of water depends strongly on the surface considered; the (001) surface of aragonite and the (10.4) surface of calcite, displaying orthorhombic and hexagonal symmetry respectively. The different adsorption patterns leads to different solvation forces when changing the surface separation. Calcite feature long decay lengths over 3 nm, in pure water, whereas the decay is much shorter in the case of the aragonite surfaces. The surface forces at short interfacial separations (< 1 nm) are dominated by the interaction of two strongly adsorbed water layers expected to be important when defining the wettability of the surfaces.

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## Study of the kinetic effects in homogeneous and heterogeneous bubble cavitation via atomistic simulations

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Cavitation is the formation of bubbles in the surrounding liquid. The formation of the liquid-vapor interface has an energetic cost which makes liquids very resilient to the growth of the new vapor/gas phase. However once formed and advected with the flow bubble give rise to extreme phenomena such as sonoluminescence [1], damage of pumps and turbines [2] and destruction of living tissues [3]. Controlling cavitation is therefore crucial in many scientific contexts. In particular, many fundamental aspect of the first stage of cavitation, the nucleation of bubbles, remain elusive and difficult to quantify.

Classical Nucleation Theory, which is based on simple continuum models, might fail to reproduce the actual nucleation rates. It is also very difficult to control the experimental conditions to tell whether cavitation is happening in homogeneous, i.e. in pure bulk liquid, or heterogeneous conditions, i.e. in presence of impurities that catalyze the process.

The nucleation event occurs on microscopic time and length scales, which makes atomistic models well suited to get insights in the phenomenon. In this work atomistic simulations are employed to study homogeneous and heterogeneous cavitation of metastable liquids at different thermodynamic conditions. Molecular dynamics is combined with Forward Flux Sampling technique [4] to evaluate the nucleation rates, allowing also the sampling of the ensemble of reactive paths. Performing a statistical analysis of the transition pathways, it is possible to assign a weight to the different reaction channels. This allows to identify which channels are kinetically preferred and which factors affect the inception of nucleation event.

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# Simulating cavitation in hydrophobic nanopores: the effect of the line tension

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The idea of attributing an energetic weight to the formation of the triple line in a biphasic system dates back to the fathers of Thermodynamics [1]. The existence of such excess energies proportional to the length of the triple line has been since then a debated topic due to the intrinsic elusiveness of this quantity. In the context of vapour nucleation at the nanoscale, it is a well known fact that the nucleation rates depend exponentially on the free energy barriers associated with the formation of a critical bubble. Line terms can therefore be probed with exponential sensitivity by experiments [2] or simulations of nucleation [5, 4]. In order to obtain quantitative information on such terms from experiments or simulations it is necessary to use a nucleation theory able to explain such phenomena at the nanoscale. The original formulation of Classical Nucleation Theory (CNT) was shown to be insufficient for the task, as it is unable to take into account nanoscale effects which become relevant when scaling down the system size. However, CNT can be endowed with terms proportional to the length of the triple line which affords a quantitative matching with nucleation data. In this work we perform MD simulations to study water vapour nucleation from a nanoporous hydrophobic material using a state-of-the-art rare-event technique, the string method in collective variables [3], in order to calculate the most probable nucleation path and the free energy barriers associated with the formation of a critical bubble. We developed a new accurate postprocessing technique able to compute, starting from atomistic data, a number of quantities: vapour volume, areas of the interfaces, and length of the triple line. This method was applied to estimate these quantities along the most probable nucleation path resulting from the string method calculations. Using these data in a modified CNT model we were able to obtain remarkable agreement with the atomistic free energy profiles. These results were obtained for negative values of the line tension of about  $-2 \cdot 10^{-11}$  N in agreement with the experimental results in [2]. We further test the validity of the line tension concept by using the value obtained from atomistic simulations in Surface Evolver calculations in which CNT is enriched with line-scaling contributions. Results are critically discussed, showing that instabilities of the liquid-vapour interface may arise.

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# The Salvinia prototype: stability and recovery of superhydrophobicity on nanotextured surface in submerged conditions

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Salvinia is a water fern which remains dry even after a long underwater immersion [1]. This feature is due to the unique surface structures covering its leaves which consist of hydrophobic re-entrant cavities with, surprising, hydrophilic patch on their top. In submerged conditions, such complex system is capable of stabilizing a confined gas layer – the so-called Cassie state – which keeps the leaves dry. The presence of the gas layer gives to the surface remarkable properties which are commonly known as superhydrophobicity. Superhydrophobic properties include, among others, the ability to reduce drag, to prevent fouling, and to avoid the formation of ice. Such properties are of utmost technological interest for submerged applications. Such properties are lost if the liquid fully wets the surface (Wenzel state) or gas bubbles cavitate and grow.

Inspired by the Salvinia, in this contribution we present molecular dynamics simulations of a simple liquid wetting a re-entrant nanotextured surface with heterogeneous chemistry (hydrophobic body and hydrophilic top layer). The Cassie-Wenzel and cavitation transitions are investigated at different thermodynamic conditions via a rare-event method which allows to quantitatively characterize the stability of the Cassie state and the kinetic of the transitions.

Results show that the re-entrant nanotextured geometry and the heterogeneous chemistry allow to obtain a more robust Cassie state over a broader region of thermodynamic conditions as compared to purely hydrophobic and hydrophilic surfaces [2]. Moreover, at negative liquid pressures (sucking), the hydrophilic top layer allows to restore the superhydrophobic Cassie state from the Wenzel state preventing the cavitation of gas bubbles [3]. To summarize, Salvinia features have allowed us to derive simple design criteria which could help the engineering of surfaces with controlled wetting properties for submerged superhydrophobicity.

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# Theoretical Principles of Self-Recovery Superhydrophobic Surfaces

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The use of hydrophobic textured surfaces, superhydrophobic for short, i.e. surfaces decorated with suitable corrugations, recently emerged as a promising passive technique to reduce the drag in macro (marine vessels, transportation of liquids in pipelines, etc.) and micro (electrokinetic batteries, Micro/Nanoelectromechanical systems (MEMS/NEMS), digital microfluidics, etc) applications. The phenomenon underneath drag reduction is that the liquid suspended on the surface textures by capillary forces (Cassie state) reduces the effective contact area with the solid. But a liquid can also completely wet the textures of a surface (Wenzel state) with the ensuing increase of drag. Cassie and Wenzel can be the stable and metastable states of a liquid on a textured surface over a wide range of conditions, and an external perturbation can bring the system in the undesired latter one (wetting transition). The reverse process is typically difficult because of large free energy barriers between Wenzel and Cassie states and, as a matter of fact, the wetting transition is considered irreversible in most (if not all) present hydrophobic textured surfaces. Many *active* approaches have been developed to induce the Wenzel-Cassie transition (e.g. hydrolysis or gas injection), but they are unpractical in applications. Thus, a passive approach in which the system spontaneously recovers the Cassie state (self-recovery) is highly sought after.

The design of self-recovery surfaces requires a deep understanding of the *phase diagram*, mechanism and kinetics of vapor/air bubble nucleation in water confined in surface textures of complex morphologies. Indeed, the problem of self recovery surfaces can be recast in terms of reduction of the distance between binodal and spinodal curves as a function of the surface textures morphology and *chemistry*. A reduction of this distance minimizes the metastability of the Wenzel state and makes self-recovery effective. The separation between the binodal and spinodal curves is function of the dependence of the Wenzel-Cassie barrier on the thermodynamic conditions and, parametrically, on the morphology and chemistry of surface textures. In my contribution I will present our recent continuum and rare events molecular dynamics analyses of the mechanism and kinetics of formation of a water vapor phase in surface textures, which is the step determining the rate of the Wenzel-Cassie transition. We considered a number of surfaces of wide experimental interest: square and circular pored, pillared and ridged surfaces. We studied the effect of their characteristic lengths (e.g. size of the pore, distance between pillars or ridge) and thermodynamic conditions on the kinetics of recovery. I show that each of these surfaces is good at either hindering the Cassie-Wenzel transition (large free energy wetting barrier) or promoting the recovery (low free energy vapor nucleation barrier in the surface textures): no one is good at both. I also show how one can combine the best characteristics of each of these surfaces to produce a modular self-recovery textured hydrophobic surface. I present the fundamental theoretical aspects underneath the characteristics of these surfaces to kinetically resist to the wetting and promote the recovery, and derive simple design principles for self-recovery hydrophobic textured surfaces.

## Electric double layer in electrode slit pores. Grand canonical Monte Carlo simulation at constant electrode potential

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Investigation of the structural and thermodynamic properties of the electric double layer (EDL) at the electrode | electrolyte interface by molecular simulations is usually carried out by the grand canonical Monte Carlo (GCMC) technique at a fixed electrode charge density. This method cannot be used to calculate the differential capacitance of EDL in electrode slit pores, the property which can be compared with the experimental results. The problem appears in calculation of the electrode potential by integrating the ion distribution in a confined system where the bulk electrolyte does not exist. Kiyohara *et al.* [1-3] have developed the GCMC technique at a constant potential drop between the anode and cathode which eliminates these difficulties. The system used to study slit pore properties was composed of three simulation boxes: separator, anodic and cathodic pores. Both walls of a slit pore had the same potential but the electrode charge was fluctuating. This fluctuation was used to assess the differential capacitance [4].

We have simplified the simulation system to one box representing a single electrode slit pore. Now the potential drop between the electrode and the bulk of an electrolyte is fixed. In the GCMC steps responsible for a particle exchange between the reservoir and the system, one ion selected at random is inserted to or removed from the simulation box. At the same time the electrode charge is changing to keep the electro-neutrality condition. These changes are employed to calculate the electrode mean surface charge density and the differential capacitance of EDL. The GCMC technique ensures the correct chemical potential of the electrolyte in pores. It means that even though the bulk of an electrolyte is not observed, its concentration is known. It was found that for the restricted primitive model of an electrolyte, with decreasing separation between walls the mean surface charge density and the differential capacitance decrease, while the concentration of counterions increases and that of coions decreases.

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## Electric Double Layer for Charged Hard Spheres With an Off-center Charge

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Recently, we proposed a relatively simple new model, charged hard spheres with an off-center charge[1], to describe an asymmetric electrolyte and reported some results for the electric double layer of such a system. Here, we report some further GCMC simulation results for double layer of this system for various distances of the ion charge from the sphere center and for charge asymmetric ions.

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# Liquid drops on surfaces: using density functional theory to calculate the binding potential and drop profiles and comparing with results from mesoscopic modelling

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For a liquid film on a solid substrate, we determine the binding potential  $g(h)$  that encodes the wetting behaviour. The method developed in [1] for a simple discrete lattice-gas model, is used with continuum density functional theory (DFT) to calculate the binding potential for a Lennard-Jones fluid and other simple liquids. The DFT we use incorporates the influence of the layered packing of molecules at the surface. In certain systems this can result in an oscillatory decay of  $g(h)$ , i.e., a structural disjoining pressure  $\Pi = -\partial g/\partial h$  [2]. The obtained binding potentials are incorporated in a mesoscopic hydrodynamic model to study the spreading of (terraced) drops on both, an adsorption (or precursor) layer and completely dry substrates [3]. To achieve this, the thin film model is modified in such a way that for thicker films the standard mesoscopic hydrodynamic theory is realised, but for very thin layers a diffusion equation is recovered.

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## Solvent fluctuations around solvophobic, solvophilic and patchy nanostructures and the accompanying solvent mediated interactions

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Using classical density functional theory (DFT) we calculate the density profile  $\rho(\mathbf{r})$  and local compressibility  $\chi(\mathbf{r})$  of a simple liquid solvent in which a pair of blocks with (microscopic) rectangular cross-section are immersed. We consider blocks that are solvophobic, solvophilic and also ones that have both solvophobic and solvophilic patches. Large values of  $\chi(\mathbf{r})$  correspond to regions in space where the liquid density is fluctuating most strongly. We seek to elucidate how enhanced density fluctuations correlate with the solvent mediated force between the blocks, as the distance between the blocks and the chemical potential of the liquid reservoir vary. For sufficiently solvophobic blocks, at small block separations and small deviations from bulk gas-liquid coexistence, we observe a strongly attractive (near constant) force, stemming from capillary evaporation to form a low density gas-like intrusion between the blocks. The accompanying  $\chi(\mathbf{r})$  exhibits structure which reflects the incipient gas-liquid interfaces that develop. We argue that our model system provides a means to understanding the basic physics of solvent mediated interactions between nanostructures, and between objects such as proteins in water, that possess hydrophobic and hydrophilic patches.

## Non-equilibrium interfaces in fluids

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The concept of non-equilibrium interfacial tension, defined via the work required to deform the system such that the interfacial area is changed while the volume is conserved, is discussed in the context of non-equilibrium fluid-fluid interfaces and of the relaxation of an initial perturbation of fluids towards the equilibrium state.

For the former case it is shown that the interfacial structure between fluid phases not at coexistence relaxes towards that of the equilibrium interface at the same temperature long before the bulk phases have been equilibrated [1].

For the latter case it is shown that the non-equilibrium interfacial tension is not necessarily positive and that the possibility of negative non-equilibrium interfacial tensions is consistent with the requirement of strictly positive interfacial tensions under equilibrium conditions [2].

Finally it is demonstrated that the presence of a negative non-equilibrium interfacial tension does *not* necessarily lead to interfacial instabilities such as finger formation. Moreover, the influence of hydrodynamic interactions on the occurrence of interfacial instabilities is analysed [3].

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# Phase diagram and critical phase transitions of driven granular matter in quasi 2d

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Driven granular matter exhibits a rich variety of nonequilibrium phases [1, 2]. Recently, a critical transition to a state with quadratic order has been reported, with several critical exponents measurable [3]. We study this set-up by computer simulations, which consists of spherical particles between two horizontal plates. The particles are agitated by vibrating the plates in vertical direction. The energy injection is balanced by energy loss through inelastic collisions of the granular particles. Thus, the system reaches a steady state which exhibits phase behavior similar to equilibrium systems. The gap between the plates is about two particle diameters allowing the particles to form - besides fluid-like states - hexagonal and quadratic bilayers. We determine the relevant parameters for formation of ordered states, present a numerical phase diagram for this system, and study phase coexistence and criticality.

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## The magic numbers of equal spheres on triply periodic minimal surfaces

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Regular structures of equal spheres on the triply periodic minimal surfaces known as primitive (P), gyroid (G) and diamond (D) surfaces are investigated by using Monte Carlo simulations of hard spheres undergoing the Alder transition. Remarkably, there exist magic numbers producing the regular structures, which are simply explained by means of *hexagulation numbers* defined as  $H = h^2 + k^2 - hk$ , in analogy with the Caspar and Klug's *triangulation numbers*,  $T = h^2 + k^2 + hk$  for icosahedral viruses, [1] where  $h$  and  $k$  are equal to nonnegative integers. Understanding the significance of symmetry of the surfaces, the total number of spheres per cubic unit cell  $N$  is represented by  $N = 8H$ ,  $16H$ , and  $32H$  for P-, G- and D-surfaces, respectively. Accordingly, these arrangements are analyzed in terms of space groups, equivalent positions (Wyckoff positions), and polygonal-tiling representations. The key is that there is only a limited number of efficient physical design possible even on the triply periodic minimal surfaces. [2, 3]

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We study sedimentation-diffusion-equilibrium and the dynamics of colloidal mixtures under gravity. In equilibrium we focus on the role of the sample height in sedimentation. To this end, we extend a recently proposed theory [1] that uniquely links the bulk phase behaviour and the sedimentation-diffusion-equilibrium of a given binary colloidal mixture. We show that in general two samples that differ only in the sample height might develop different phases under gravity, that is, different sequences of stacks of distinct layers [2]. As an example of recent interest, we apply our theory to study sedimentation in patchy colloidal mixtures where we observe an extremely rich phase behaviour. We conclude that the sample height is, in general, an essential control parameter in sedimentation.

Additionally, we study the dynamics of colloidal mixtures under gravity using power functional theory (PFT) [3] and Brownian dynamics simulations. PFT is the exact extension of equilibrium density functional theory for treating non-equilibrium dynamics of many-body Brownian systems. We focus on a binary mixture of hard spheres. By varying the gravitational length we find different non-equilibrium phases such as lane formation and homogeneous diffusion.

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# Diffusion in Quasi-One Dimensional Channels: A Small System Isobaric-Isothermal (n, p, T) Transition State Theory for Hopping Times

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Brownian particles confined to narrow, quasi-one dimensional channels exhibit a dynamic transition from single file diffusion (SFD) to normal diffusion as the channel diameter reaches a passing threshold where the particles are able to hop past each other [1, 2]. In this crossover regime, molecular simulations have shown that the long time diffusion coefficient of the particles can be described in term of a hopping time, defined as the average time a particle performs SFD before escaping the cage formed by its neighbours [1, 3]. We use a small system isobaric- isothermal, NPT, ensemble to develop a rigorous Transition State Theory approach for calculating the hopping time that involves calculating the free energy barrier associated with two particles attempting to pass [4]. The method is then used to explore how particle-particle and particle-wall interactions influence diffusion in narrow channels, including studying the possibility of using the SFD-Normal diffusion crossover regime for the dynamic separation of mixtures.

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The dynamic adsorption process of particles at surfaces (or interfaces) addresses fundamental questions as well as has several applications (smooth coatings, functionalized surfaces, efficient organic solar cells) [1]. This dynamic adsorption leads to evolution of thin films mainly consisting anisotropic particles and is observed in the self-assembly of organic monolayers [1], growth of organic semi-conductors thin films by deposition [2, 3] etc.

We investigate the phase behavior of equilibrated structures of rod-like particles near a substrate as well as their dynamic deposition using "dynamic" Monte-Carlo (MC) simulations. We compare our MC data to density-functional theory and kinetic MC simulations [4, 5]. We also write rate equations (REs) for film growth of organic rod-like particles inspired by adatom attachment-detachment film growth model [6].

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Stokes' law describes the friction exerted on a macroscopic solute from flowing solvent particles, using the hydrodynamics with a boundary condition on the solute surface. Although Stokes' law is believed to be valid for a macroscopic solute, it is not clear whether it can be understood on the basis of Hamiltonian particle systems. In particular, when microscopic solute-solvent interaction depends solely on the particle distance, there are arguments about derivation of the boundary condition. Some studies, such as molecular dynamics simulations, have shown the slip boundary condition, while other studies have shown the stick boundary condition. In the present study, to determine the boundary condition in Stokes' law by the microscopic Hamiltonian, a theory is developed on the basis of our previous studies [1–4].

First, the slip boundary condition is exactly derived when the solute-solvent particle interaction depends solely on the distance between particles. The boundary condition is derived from the Hamiltonian equations including interaction between all solvent particles and a solute. In these equations, the macroscopic-solute limit of  $\sigma/R \rightarrow 0$  is taken, where  $\sigma$  and  $R$  are the sizes of a solvent particle and solute. The result is independent of particle interaction and solvent particle density.

In addition, in cases of more general solute-solvent interaction, from the Hamiltonian equations, a boundary condition is obtained by

$$\frac{\partial v_\theta(\mathbf{r})}{\partial r} - \frac{v_\theta(\mathbf{r})}{R} = \frac{v_\theta(\mathbf{r})}{\delta}, \quad (1)$$

at  $r = R$ , where

$$\frac{1}{\delta} = \frac{1}{4\pi R^2 \eta k_B T} \int_0^\infty dt \langle F_\theta^{tot}(t) F_\theta^{tot}(0) \rangle_{eq}. \quad (2)$$

Here,  $v_\theta(\mathbf{r})$  is the tangential component of the velocity field of solvent particles, where the origin of the polar coordinate system is located at the center of the solute. In addition,  $\eta$  is the shear viscosity, and  $F_\theta^{tot}(t)$  is the tangential component of the total force exerted from all solvent particles on the solute. The equations are valid even when the solute consists of many particles with internal motions. Using the equations, the macroscopic friction can be calculated by a microscopic correlation function, which is equivalent to that obtained in a flow past a flat solid interface.

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## Tricritical Casimir forces and order parameter profiles in wetting films of $^3\text{He}$ - $^4\text{He}$ mixtures

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Tricritical Casimir forces in  $^3\text{He}$  -  $^4\text{He}$  wetting films are studied, within mean field theory, in terms of a suitable lattice gas model for binary liquid mixtures with short-ranged surface fields. The proposed model takes into account the continuous rotational symmetry  $O(2)$  of the superfluid degrees of freedom associated with  $^4\text{He}$  and it allows, inter alia, for the occurrence of a vapor phase. As a result, the model facilitates the formation of wetting films, which provides a strengthened theoretical framework to describe available experimental data for tricritical Casimir forces acting in  $^3\text{He}$  -  $^4\text{He}$  wetting films [1, 2].

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# Onset of anomalous diffusion in colloids confined to quasi-monolayers

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A colloidal monolayer, e.g., formed at a fluid interface or by means of a suitable confining potential, exhibits anomalously fast collective diffusion [1, 2]. This effect, also observed experimentally in a strong increase of the wavenumber ( $k$ ) –dependent diffusion coefficient for  $k \rightarrow 0$  [3], is a consequence of the hydrodynamic interactions mediated by the three-dimensional (3D) ambient fluid acting on the confined particles. We study theoretically and with numerical simulations [4] the crossover from normal to anomalous diffusion as the particles are, in real systems, confined by a 3D external potential and thus have the possibility to fluctuate out of the 2D manifold, thus forming actually a quasi-monolayer.

Hydrodynamic interactions are approximated by their far-field limit at the two-body level, introducing a characteristic length scale  $L_{\text{hydro}}$ . Denoting the width of the confinement by  $\ell_C$ , we have two competing lengthscales in our system and thus identify three different regimes: On scales much larger than the width of confinement  $\ell_C$  and the characteristic length  $L_{\text{hydro}}$ , the collective diffusion in the monolayer is always anomalous. For scales below  $L_{\text{hydro}}$ , the density evolution follows 2D normal diffusion, and for scales below  $\ell_C$ , the 3D normal diffusion is recovered. An important consequence is that *all* collective diffusion processes of quasi-monolayers in an ambient fluid become anomalous since the lateral scale becomes larger than both  $\ell_C$  and  $L_{\text{hydro}}$  at long times. This would apply e.g. to interfacially trapped colloids or Marangoni flow of surfactants.

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## Solvent mediated forces in critical fluids

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Effective interactions between particles immersed in a fluid have been the subject of extensive investigations in different regimes: from the Asakura-Oosawa short range attraction present in the ideal gas limit, to the oscillatory behavior induced by repulsive forces. These depletion interactions represent a particular limit of the more general concept of solvent mediated forces, which are known to drive several important phenomena in soft matter, leading either to clustering, colloidal aggregation or dynamical arrest.

Solvent mediated forces undergo a significant change when long range correlations are present in the host fluid due to the proximity of a second order phase transition. The universal properties of critical phenomena reflect in the structure of the effective interactions, which acquire a scaling form [1]. The transition between the depletion and the critical Casimir regimes is a particularly challenging problem from the theoretical point of view because it requires the accurate description of inhomogeneous critical fluids at a microscopic level.

To achieve this goal, we developed a novel density functional technique based on the weighted density concept [2]. Coupling this approach with the hierarchical reference theory of fluids (HRT) [3], which provides a microscopic description of fluids accurate also in the critical region, we performed a detailed investigation of the effective interactions between two hard walls immersed in a Yukawa fluid by varying the thermodynamic state.

The evolution of the effective potential as a function of temperature and density is discussed, emphasizing the smooth transition between the high temperature, entropy-dominated, limit and the critical regime. Furthermore this approach allows a direct investigation of the universal properties both in the critical and in the pre-critical regime and these results are compared with predictions obtained by numerical simulations [4, 5].

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## Drag coefficient of a raft-like domain having the membrane viscosity different from the one outside the domain

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We calculate the drag coefficient of a raft-like circular liquid domain in a flat fluid membrane, whose viscosity inside the domain is different from that outside the domain. As mentioned below, we note the continuity of the two-dimensional stress tensor at the domain boundary, and obtain the drag coefficient as a power series with respect to a dimensionless parameter  $\kappa = 1 - \eta_o/\eta_i$ , where  $\eta_o$  and  $\eta_i$  are the membrane viscosities outside and inside the domain, respectively.

For a sufficiently slow motion of the domain, the force acting on the domain is proportional to its speed, and the constant of proportion is referred to as drag coefficient. In this linear regime, the domain is assumed to be circular. The drag coefficient is calculated for a rigid disk [1, 2], and for the domain whose viscosity is the same as the one outside the domain [3]. The former case ( $\kappa = 1$ ) is utilized in experiments about the diffusion of a membrane protein in a lipid bilayer [4, 5], while the latter ( $\kappa = 0$ ) is applied in experiments of an artificial membrane [6]. However, when the viscosities inside and outside the domain are different, the calculation has been performed only up to the linear order with respect to  $\kappa$  [7, 8].

Here, we obtain the drag coefficient as a power series with respect to  $\kappa$  by employing the continuity of the stress tensor as in [8], unlike in [9]. For  $\eta_i \neq \eta_o$  the continuity of the velocity gradient at the domain boundary is not automatically fulfilled. Thus we have to consider not only the single-layer but also double-layer potentials. We obtain recurrence relation of the coefficients in the power series. It is numerically found that the series can be well estimated by truncation up to the first 40 terms at the most, and the results with  $\kappa = 1$ , *i.e.*  $\eta_i \rightarrow \infty$ , agree well with the case of the rigid domain in [1]. Part of the detail of our calculation can be seen in preprint [10].

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## Dynamical behavior of hydrated water molecules between phospholipid membranes

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Biological molecules such as nucleic acids, proteins, and carbohydrates are surrounded by water molecules and their biological functions can only be realized in relation with water. The importance of elucidating the structure and dynamics of water molecules near biological molecules is widely recognized. Here we investigated the dynamical behavior of hydrated water sandwiched between 1,2-dimyristyl-sn-glycero-3-phosphocholine (DMPC) bilayers by quasi-elastic neutron scattering (QENS). [1]

The experiments were carried out at Time-of-Flight near backscattering spectrometer DNA at the Japan Proton Accelerator Research Complex (J-PARC) in Tokai, Japan. The energy resolution was  $\sim 3.6 \mu\text{eV}$  using Si 111 analyzer. The initial proton beam incident power on the neutron target was about 300kW. Perdeuterated lipid was mixed with  $\text{H}_2\text{O}$  in order to investigate the dynamical behavior of water molecules.

The results revealed that the hydrated water could be categorized into three types of water: (1) free water, whose dynamical behavior is slightly different from that of bulk water; (2) loosely bound water, whose dynamical behavior is one order of magnitude slower than that of the free water; and (3) tightly bound water, whose dynamical behavior is comparable with that of DMPC molecules. The number of loosely bound and tightly bound water molecules per DMPC molecule decreased and increased with decreasing temperature, respectively, and the sum of these water molecules remained constant. The number of free water molecules per DMPC molecule was constant in the measured temperature range. These results indicate that the hydration of lipid molecules changes monotonically with temperature and is independent of the structural transition of lipid bilayers.

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# Transient Casimir Forces from Quenches in Thermal and Active Matter

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We compute fluctuation-induced (Casimir) forces for classical systems after a temperature quench [1]. Using a generic coarse-grained model for fluctuations of a conserved density, we find that transient forces arise due to long-ranged non-equilibrium correlations, even if the initial and final states are force free.

In setups reminiscent of Casimir (planar walls) and van der Waals (small inclusions) interactions, we find comparable exact universal expressions for the force. Dynamical details only scale the time axis of transient force curves.

We propose that such quenches can be achieved, for instance, in experiments on active matter, employing tunable activity or interaction protocols.

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We describe the mechanism of the nucleation and growth of the inclusions (droplets) of the nematic or isotropic phase in the free-standing smectic films (FSSF) overheated above the temperature of the bulk smectic - nematic (isotropic) transition. Our approach is based on the general thermodynamic theory of the stability of the smectic films upon the change of the external conditions [1]. We determined conditions under which the drops nucleation is favorable in the overheated FSSF. The values of the critical work for the drops formation and the critical size of the drops have been calculated. We have shown that the formation of droplets in overheated FSSF is only possible in the presence of a large amount of thermally generated dislocation loops. The spreading out of dislocation loops provide necessary material for the drops formation and initial stage growth. The further drops growth can occur through merging of the smaller drops with the larger one.

To specify the mechanism of the drops coalescence in the overheated FSSF, we considered the role of the main interactions - attractive and repulsive - between them. The above coupling is a special case of colloidal interactions, where the nematic (isotropic) inclusions in smectic medium represent the different phase state of the same material [2]. We have derived at first time the analytical expression for the capillary attraction force between spontaneously formed droplets arising due to gradients of the surface energy in the area between the drops. The estimations of the characteristic distances at which the drops coalescence is possible have been made. We considered also the classic dispersion forces, as well as the long-range "pseudo-Casimir" interaction, originating from the thermal Goldstone modes of the confined correlated media. The calculation of the drag force for the movement of the spherical (lens-like) droplet in FSSF is made in the frame of the general hydrodynamic theory and dynamics of smectics in the limit of the small Reynolds number for the movement of the spherical object. The corresponding calculations were made neglecting the leakage between the smectic layers and taking the possible slipping at the drop surface into account. The influence of the shape of the drops that can change from spherical (isotropic drops) to more spread out, bell-like (nematic inclusions) on the character of their interaction is also investigated. Our theoretical calculations are in good agreement with the known experimental observations.

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# Enhanced wavelength-dependent surface tension of liquid–vapour interfaces

7.060

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Due to the simultaneous presence of bulk-like and interfacial fluctuations the understanding of the structure of liquid–vapour interfaces poses a long-lasting and ongoing challenge for experiments, theory, and simulations. We provide a new analysis of this topic by combining high-quality simulation data for Lennard-Jones fluids with an unambiguous definition of the wave-number-dependent surface tension  $\gamma(q)$  based on the two-point correlation function of the fluid [1]. Upon raising the temperature from that of the triple point to that of the liquid–vapour critical point,  $\gamma(q)$  develops a maximum at short wavelengths. We compare these results with predictions from density functional theory. Our analysis has repercussions for the interpretation of grazing-incidence small-angle X-ray scattering (GISAXS) at liquid interfaces.

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In this work, we examine the effect of a surface phase transition on the wetting and spreading of liquid droplets. In a recent work [1] we reported molecular-dynamics (MD) simulation results that predict a solid-liquid premelting at the Al(*s*)/Pb(*l*) interface at temperatures just below the melting point of Al. In addition, we show for the Al(111) surface that, although the Al(111)/Pb solid-liquid interface exhibits premelting, the Al(111) free surface does not. Therefore, the spreading of Pb(*l*) droplets on an Al(111) surface will be coupled to a concurrent spreading of the premelting layer underneath. In an extensive series of MD simulations of the spreading of hemicylindrical Pb droplets on Al(111), we analyze both the dynamics of the spreading and the equilibrium wetting properties of the droplet. The simulations show that, at long times, the droplet radius  $R(t)$  relaxes exponentially to its equilibrium value, in agreement with theory for systems, such as this one, where the droplet only partially wets the substrate [2]. For intermediate times, the radius is expected to scale according to a power law [ $R(t) \approx t^{1/n}$ ], where, for a cylindrical geometry,  $n = 7$  for a *hydrodynamic* mechanism in which the dominant energy dissipation is viscous relaxation of the fluid droplet and  $n = 5$  for a *kinetic* mechanism in which frictional dissipation at the interface is dominant [3, 4]. Our simulations show that spreading on the premelted surface is consistent with the kinetic mechanism. If premelting is inhibited, either by artificially freezing the surface or by examining spreading at temperatures below the Al(111) roughening transition, where the substrate is faceted, the simulations show scaling laws consistent with the hydrodynamic mechanism. Also, the existence of the premelting layer significantly reduces the wetting contact angle over that for the frozen or faceted surfaces. Therefore, we conclude that the presence of the surface phase transition (premelting) qualitatively and quantitatively alters the spreading mechanism and equilibrium wetting of droplet spreading of Pb(*l*) droplets on a Al(111) surface. In addition, the structure of the droplet-substrate interface, with its four-phase contact region, is shown to resemble closely that usually associated with reactive wetting.

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## Temperature dependence of surface tension of 1-butanol aqueous solution

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Surface tension of most liquids decreases as temperature increases, but surface tension of dilute aqueous solutions of high carbon alcohols (number of carbon atoms  $\geq 4$ )[1] or liquid metal alloys such as Sn-X (X=Ag,Cu)[2] increases as temperature increases in certain temperature and concentration conditions. This feature has attracted a lot of attention because it is relevant to rich thermocapillary behavior such as anomalous Marangoni convection[3] or enhanced heat transfer[4]. Based on the thermodynamics of interfaces, change of surface tension is described as a competition among surface entropy, surface excess and chemical potential of solute. However, it is not understood that which property play crucial role when temperature derivative of surface tension become positive. In the present work, we focus on 1-butanol aqueous solution as a typical liquid which shows positive value of temperature derivative of surface tension. All-atom molecular dynamics simulations are performed to understand thermodynamic mechanism of temperature dependence of surface tension of 1-butanol aqueous solution. The surface tension and surface excess are computed at fixed temperature and molar concentration of the solution and orientation of 1-butanol molecules at interface is analyzed. Temperature dependence of surface tension is discussed based on thermodynamic relation.

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## Stretching of viscoelastic drops by steady sliding

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Controlling and manipulating drops on open surfaces is a crucial step for applications in many fields, including chemistry, biomedicine, ink-jet printing, food and pharmaceutical industry [1, 2, 3]. The vast majority of such applications involve non-Newtonian fluids, e.g. polymer solutions, biological samples, blood or inks, characterised by a non-linear response to external stresses, consisting either in a shear dependent viscosity (shear-thinning, shear-thickening or yield stress fluids) or in elastic effects related to the appearance of normal stresses. Despite the wide spread of complex fluids, the research about the behaviour of non-Newtonian drops is quite recent and limited mainly to spreading [4, 5], dynamic wetting [6, 7], and impacting [8] on surfaces.

The sliding of non-Newtonian (liquid) drops down planar surfaces results in a complex, entangled balance between interfacial forces and non linear viscous dissipation, which has been scarcely inspected. In particular, a detailed understanding of the role played by the polymer flexibility and the resulting elasticity of the polymer solution is still lacking, but of paramount importance for surface science and related technology. To this aim, we have considered polyacrylamide (PAA) solutions, with different molecular weights, suspended either in water or glycerol/water mixtures [9]. Side by side comparisons between the sliding with stiff and flexible polymers have been extensively worked out. Drops with flexible polymers may exhibit a remarkable elongation in steady sliding, which is not observed in drops with stiff polymers, most likely due to the reduced viscous bending of the corresponding shear-thinning solution. Moreover, an “optimal elasticity” of the polymer seems to be required for this drop elongation to be visible. We have complemented experimental results with numerical simulations of a viscoelastic FENE-P drop. This has been a decisive step to unravel how a change of the elastic parameters (e.g. polymer relaxation time, maximum extensibility) reflects in the dimensionless sliding velocity.

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## Critical adsorption on a line defect

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We investigate the critical adsorption on a line defect, in the three-dimensional Ising universality class, by means of Monte Carlo simulations of an improved lattice model, where the line defect is modeled by a local line field coupled to the order parameter. We show that the model exhibits a crossover behavior from the zero line-field to a critical adsorption fixed point. In line with field-theoretical results, we find that at the critical adsorption fixed point the short-distance expansion of the order-parameter profile exhibits a new universal critical exponent, which we compute. This result also implies the presence of slowly-decaying scaling corrections, which we analyze in detail. The system can be experimentally realized by considering a rodlike particle immersed in a fluid at criticality. Moreover, this setup describes the finite-size scaling behavior in the so-called pinning-field approach, a recently advocated simulation scheme that employs a local order-parameter pinning field to study quantum critical phenomena.

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## Electrolytes between dielectric charged surfaces: Simulations and theory

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We present a simulation method to study electrolyte solutions in a dielectric slab geometry using a modified 3D Ewald summation[1]. The method is fast and easy to implement, allowing us to rapidly resum an infinite series of image charges. In the weak coupling limit, we also develop a mean-field theory which allows us to predict the ionic distribution between the dielectric charged plates. The agreement between both approaches, theoretical and simulational, is very good, validating both methods. Examples of ionic density profiles in the strong electrostatic coupling limit are also presented. Finally, we explore the confinement of charge asymmetric electrolytes between neutral surfaces.

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Particles on surfaces are found both in nature and in the lab in the form of *e.g.* proteins in membranes or colloids adsorbed to a substrate or an interface. Curved surfaces are particularly interesting, because (i) typically these surfaces simply are not flat in nature and (ii) new physics may arise especially in the case of finite surfaces such as the surface of a sphere. Disks/spheres on spherical surfaces have been considered in experiments, (numerical) continuum theory and computer simulations [1, 2, 3, 4, 5, 6]. More recently, also non-spherical particles on spherical surfaces were considered [7, 8]. Nevertheless, most of these works deal with spheres/disks on a sphere at infinite pressure (close packing); in contrast, we will consider the more interesting case of finite pressure, other particles than disks/spheres and other background spaces [9].

Here, we will present a classical density functional theory for two-dimensional hard particles on a two-dimensional curved surface. The theory is similar to the highly successful fundamental measure theory for three dimensional systems. The derivation is particularly elegant in two dimensions; we do not require any adjustable constants. We obtain analytical results for the homogeneous fluid of arbitrary convex particles on a surface with homogeneous curvature; the only two surfaces of this kind are the sphere and the hyperbolic plane. The latter surface can be approximately embedded in three dimensional space as a triply periodic minimal surface such as the gyroid, which can be formed by lipid membranes. The theory also applies to inhomogeneous systems, but the numerical implementation is nontrivial in that case and has not yet been performed. We compare to available theoretical or computer simulation results [1, 2, 9]. Previous theoretical approaches are either numerical or not as general as our theory. The analytic equation of state allows one to calculate, for example, the number of small spheres absorbed to a larger sphere in chemical equilibrium with a homogeneous fluid of small spheres with a known density (as is generally the case in experiments).

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One of molecular simulation's aims is to assess the range of validity of simple laws at the nanoscale. Gibbs' classical theory of thermodynamics divides a system free energy in bulk, surface and line contributions. Each component consists in an intensive parameter namely a pressure, a surface tension and a line tension multiplied by an extensive quantity respectively a volume, an area and a length. Although highly practical, this continuous approach, may fall down at the molecular scale where granularity of matter becomes significant.

Line tension contribution is often considered to explain heterogeneous nucleation rates or colloid adsorption [1, 2]. Yet, the order of magnitude and the sign of this parameter is still questionable as well as its underlying physics. Recent simulations even suggest that it could be of importance only at the molecular scale, where continuous modeling may break down.

Results found in the literature, based on numerical simulations, vary between  $10^{-10}$  and  $10^{-12} Jm^{-1}$  and are both positive and negative [3, 4]. The large majority of works devoted to the study of line tension rely on shape recognition of interfaces that become more and more relatively thick and blur with size reduction [3, 4]. To tackle this obstacle, we have developed a numerical measure based on anisotropic heterogeneous virial expression of free energy derivatives in the case of confined biphasic systems. This approach directly provides thermodynamic tension and avoids shape recognition. Our method provides a direct measurement of confined interface free energy, that may be compared to Gibbs theory. Continuous modeling holds down to confinements of the order of the nanometer for water or two diameters in the case of Lennard Jones fluids, and line tension is found to be of the order of  $10^{-12} Jm^{-1}$ . This approach allowed us to study the impact of structuration and hydrophobicity of the solid.

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We employ computer simulation to study the additive enhanced crystal growth in a binary Lennard Jones mixture under different scenarios. The crystal growth rate, the structure of the liquid solid interface and the interface morphologies strongly depend on the miscibility of the components. An accelerated crystal growth is observed for systems of poor solubility. We find the growth of different types of crystals and the growth dynamics depend on the structure of the interface which is determined by the solubility of the (non-crystalizing) minority component. It is also observed that the crystal growth mechanism follows the predictions of the Kardar-Parisi-Zhang theory in  $2 + 1$  dimensions for well miscible Lennard Jones mixtures.



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Hydrophilic surfaces, such as planar lipid membranes, are governed by repulsive forces at nanometer separations in aqueous solution that are not captured within classical continuum theories. Marcelja and Radic [1] were the first to propose that water orientation causes a significant contribution to the interaction free energy, however depending on the boundary conditions this model predicts either attraction or repulsion [2]. It is common consensus that the atomistic degrees of freedom need to be considered explicitly, which in simulations makes it necessary to account for the water chemical potential [3]. Using the water dipole orientation as order parameter [4] we derive the interaction parameters from bulk water properties and predict the indirect membrane repulsion quantitatively without free parameters.

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# Fluid-Solid Interactions in Nanoporous Media: From Condensation-Induced Deformations and Capillarity-Driven Transport to Switchable Imbibition

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Fluids confined in pores a few nanometers across play a dominant role in phenomena ranging from clay swelling, frost heave, oil recovery and catalysis, to colloidal stability, protein folding and transport across artificial nanostructures, bio-membranes and tissues [1]. In nanoporous solids, tight spatial confinement, solid-fluid interactions and complex pore morphologies may significantly alter the fluid's physical equilibrium and non-equilibrium properties, causing, for example, the molecular structuring of the fluid, disjoining pressures, changed shear viscosities or microscopic and macroscopic mechanical deformations of the confining host materials. Here we will present experiments and phenomenological models on capillary condensation [2], the capillarity-driven transport [3, 4] and self-diffusion [5] of liquids in nanoporous hosts, the interplay of macroscopic deformation of these hosts upon vapour and capillary condensation [6, 7] as well as a study on the influence of electrically-switchable wettability on liquid imbibition in a nanoporous gold sponge [8].

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## Molecular simulation of aqueous electrolytes in nanoporous carbons: Blue Energy and water desalination

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When fresh water comes into contact with salty water, a considerable amount of energy is dissipated [1]. Conversely, the desalination of sea water requires a lot of energy. Current processes exploiting this difference in osmotic pressure are based on transport through membranes, with limited efficiency. A new approach has recently been proposed [2] to harness this "blue energy", thanks to the charge / discharge of electrodes in electrolytes with high / low salt concentration. The use of nanoporous carbon electrodes seems promising, but the traditional models (such as Poisson-Boltzmann) used to determine the relevant quantities [3, 4] do not apply in this case where molecular interactions play an essential role.

We overcome this difficulty by performing molecular dynamics simulations of nanoporous carbon electrodes [5, 6] in the presence of an aqueous electrolyte. We evaluate the electrical capacity and the amount of ions adsorbed inside the electrodes as a function of the potential difference between the electrodes. In addition, these simulations should allow us to understand the microscopic mechanisms leading to the storage of the charge, the effect of the structure of the carbon electrode, the salt concentration in the electrolyte and the chemical nature of the salt. We will also determine the diffusion coefficients of water and ions and electrical resistance of the solution inside the electrodes.

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We report classical density functional theory and Monte Carlo computer simulation studies of SPC/E water [1] and a (truncated) Lennard-Jones liquid [2] near a weakly attractive smooth wall. As the wall-fluid attractive strength is reduced at vapor-liquid coexistence, the contact angle  $\theta$  increases towards the value  $\theta = 180^\circ$  at which drying occurs. Measurements of the local compressibility point to a diverging correlation length for density fluctuations parallel to the wall, indicating that drying is a surface critical phenomenon. For a van der Waals wall-fluid potential we find strong evidence that critical drying occurs at zero attractive wall strength, ie. in the limit of a hard wall. Our simulations yield new insight into the important role of finite-size effects on critical surface phase transitions.

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## Interplay between the critical Casimir and dispersion forces in ellipsoid/sphere - plate systems immersed in non-polar fluid

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Here we study systems with simultaneous occurrence of both the long-ranged van der Waals and critical Casimir forces. As the first are of quantum origin and hence are invariably present in any real physical system, the last arise as an effective interaction between objects when immersed in a near-critical medium, say a non-polar one-component fluid or a binary liquid mixture. They are due to the boundaries of the bodies, which modifies the order parameter profile of the medium between them as well as the spectrum of its allowed fluctuations. More specifically, we study the net total force (NTF) between an ellipsoidal or spherical in shape colloidal particle and a thick planar slab. We do that using general scaling arguments and mean-field type calculations utilizing the Derjaguin and the surface integration approaches. They both are based on data of the forces between two parallel slabs separated at a distance  $L$  from each other, confining the fluctuating fluid medium characterized by its temperature  $T$  and chemical potential  $\mu$ . The surfaces of the colloidal particles and the slab are coated by thin layers exerting strong preference to the liquid phase of a simple fluid, or one of the components of a mixture, modeled by strong adsorbing local surface potentials, ensuring the so-called (+;+) boundary conditions. On the other hand, the core region of the slab and the particles, influence the fluid by long-ranged competing dispersion potentials. We demonstrate that for a suitable set of colloid-fluid, slabs-fluid, and fluid-fluid coupling parameters the competition between the effects due to the coatings and the core regions of the objects involved result, when one changes the temperature  $T$ , the chemical potential of the fluid  $\mu$ , or the distance  $L$  between the objects, in *sign change* of the NTF acting between the colloids and the slab. The last can be used for governing the behavior of objects, say colloidal particles, at small distances, say in colloid suspensions for preventing flocculation. It can also provide a strategy for solving problems with handling, feeding, trapping and fixing of microparts in nanotechnology.

# The effect of spatial confinement on the phase behavior of Heisenberg fluids

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In recent years ferrofluids have been used in both commercial applications and scientific studies. Often these suspensions of magnetic particles are subject to spatial confinement to make use of their unique properties[1, 2].

To describe the behavior of such confined suspensions on the theoretical level we employ classical density functional theory (DFT) to investigate equilibrium properties of a pure Heisenberg fluid confined to nanoscopic slit pores of variable width. The Heisenberg fluid is modelled as a spherical particle with a hard core and an additional isotropic Lennard-Jones potential. We further modify the potential to include attractive interactions between classical three-dimensional spins. Within DFT pair correlations are treated at modified mean-field level and the free energy of the hard sphere reference fluid is described with fundamental measure theory.

Based on a previous study on systems with nonlocal density we investigate the case of confinement between hard walls of varying width[3]. Special attention is given to the effect that the local density has on the polarisation profile across the slit pore.

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## Friction at the interface between solid self-assembled monolayers and liquid polymers or solid metal nanotips

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The friction between a solid and a liquid was historically assumed to be so large that fluid molecules in contact with a solid boundary were stuck. Thus, the classical no-slip boundary condition was applied. With the advent of micro- and nano-fluidics in the last decades, however, this boundary condition has been observed to fail in many instances. Particularly, as will be discussed here, a slip boundary condition is observed when unentangled polystyrene (PS) dewets from a hydrophobic, alkylsilane self-assembled monolayer (SAM). This boundary condition can furthermore be tuned over an order of magnitude by subtly changing the SAM [1], indicating that the friction between solid and liquid is highly sensitive to atomic level details. We have also investigated the friction between these same SAMs and a solid metal tip of nanoscopic dimensions. Remarkably, this apparent solid/solid friction is velocity dependent and exhibits a crossover from a linear to logarithmic scaling in the velocity [2]. The results can be described in terms of a distribution of nanocontacts with very weak stiffness compared to the expected one for metal/solid contacts. *The work presented here has been done in collaboration with the authors of refs. [1, 2].*

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## Experimental study of snow and ice friction

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Ice and snow friction have been an important subject of study in the last century: although the main parameters affecting ice friction have been investigated [1], very little is available about snow [2]. Indeed, because of its nature, experiments on snow are more difficult to achieve. Nevertheless, understanding snow friction is still a crucial topic for example for winter sports applications or the development of more effective means of transport.

We have designed two different experimental setups: a tribometer made of a rotating disk is filled with a 5cm thickness of snow or ice. We measure the friction force exerted on a slider mounted on top of the disk via a torque sensor. The tribometer is placed in a cold room whose temperature can be varied between -30°C and 5°C. Snow is fabricated and kept in the chamber.

We also use an in-house macroscopic (20cm long) aluminum tuning fork as force and friction sensor to investigate the properties of ice and snow: the shift in frequency and the broadening of the quality factor give important informations about the conservative and dissipative forces at stake. With these two experiments we characterise the importance of the main physical parameters involved in snow and ice friction (hardness, thermal conductivity and hydrophobicity) for different velocities and temperature regimes.

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## Mean-field theory of adsorption induced deformation of mesoporous materials.

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Adsorption of gas molecules onto the surface of porous medium induces the stress which in turn causes the strain. The deformation can either be swelling or contraction of adsorbent. First macroscopic experiments were done in the beginning of 20's century, using the optical lever extensometry authors had shown the deformation of charcoal induced by the adsorption of carbon dioxide [1]. Up to nowadays, there is a significant number of experimental studies performed by different methods such as optical lever extensometry, dilatometry and SAXS [2]. In the last decade arising interest stimulated the development of theoretical models of adsorption-induced deformation for microporous and mesoporous materials such as a poroelastic approach [3] or a thermodynamic approach based on salvation pressure [4].

In this contribution, we present a new theoretical approach of adsorption-induced deformation of mesoporous materials. The model is based on the approximation that adsorbed phase is the same as the bulk liquid at saturation and on the application of an effective potential of interaction between adsorbent and adsorption film to its surface. The deformations are treated through Hook's law. The assumption of complete wetting allows avoiding the usage of interfacial energy of solid adsorbent. The result of the model is a system of self-consistent equations describing the deformation and the adsorbed amount simultaneously. The equation for the critical capillary radius is similar to previously used ones for the description of rigid materials [5]. We test the model against the experimental data from the literature and show qualitative agreement with both deformation and adsorbed amount. Also, the calculated elastic modulus and average pore size diameter are in agreement with previously reported values in the literature.

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Thermo-osmotic slip – the flow induced by a thermal gradient along a surface – is a well-known phenomenon, but curiously there is a lack of robust molecular-simulation techniques to predict its magnitude. Here, we compare three different molecular simulation techniques to compute the thermo-osmotic slip at a simple solid-fluid interface. Although we do not expect the different approaches to be in perfect agreement, we find that the differences are barely significant for a range of different physical conditions, suggesting that practical molecular simulations of thermo-osmotic slip are feasible.

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# Molecular Simulations of Surfactant Adsorption and Self-assembly under Static and Shear Conditions

7.079

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Lubricant additives are essential in the automotive industry to ensure the smooth operation of modern engines by reducing friction, wear, oxidation, and corrosion, as well as providing thermal stability and removing debris. Many additives are organic and amphiphilic, which means that they can form aggregates in aqueous and non-aqueous solvents. In this work, large-scale atomistic molecular dynamics (MD) simulations are used to study the competition between adsorption and self-assembly in solutions of typical additives under strong confinement between inorganic surfaces, under both static and shear conditions. It is found that in non-aqueous solvents under static conditions, lubricant additives and their mixtures can form stable reverse micelles. With the application of shear, the reverse micelles disintegrate and the additive molecules partially adsorb on to the surfaces, which should translate in to complex tribological properties. In aqueous solutions of cetyltrimethylammonium bromide (CTAB) confined between mica surfaces, it is found that CTAB forms micelles or layered structures, depending on the concentration [1]. The CTAB simulations shed light on a range of recent experimental measurements [2].

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## The influence of the topological defects in the two dimensional melting

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The melting of crystal phases in two-dimensional systems has been the subject of a large amount of theoretical, numerical and experimental works. Several mechanisms to describe the melting in two-dimensional, including, in particular, the KTHNY theory and the melting induced by formation of grains boundaries, have been proposed. There are strong evidences that the melting in two dimensions depends crucially on the form and range of the interaction potentials between particles.

In this contribution, we report extensive Monte Carlo studies of the melting of the classical two-dimensional crystal for systems of point particles interacting via the  $1/r^n$  potential [1, 2] for  $n = 1, 2$  and  $3$ ; the long ranged interaction is taken into account with the Ewald method [3, 4]. For the Wigner crystal ( $n = 1$ ), a hexatic phase is found in large enough systems. With the multiple histograms method and the finite-size scaling theory, we show that the fluid/hexatic phase transition is weakly first order. No set of critical exponents, consistent with a Kosterlitz-Thouless transition and the finite-size scaling analysis for this transition, has been found.

The statistical analysis of the topological defects and of the unbinding transitions of the dislocations and disclinations pairs permit to obtain a better description of the two dimensional melting.

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# Non-equilibrium phase behavior of sheared confined molecular films under pressure using Nonequilibrium Molecular Dynamics

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Non-equilibrium Molecular Dynamics (NEMD) simulations of confined Lennard-Jones films at high pressure and large shear rates have been carried out, [1] which follows on from previous work on the extreme shearing of simple liquids [2, 3, 4, 5]. The objective of these studies was to gain insights into the physical behaviour of real liquids under comparable conditions, such as is found in high pressure lubrication in engine gears. The focus of the study is on thick films in which the nonequilibrium phases formed in the confined region impacts on the traction properties. The NEMD nonequilibrium phase and tribological diagrams are mapped out as a function of applied pressure, wall sliding speed, wetting characteristics and atomic scale surface roughness.

Depending on the range of applied pressure and shear it is found that the shear velocity profile in the gap can depart significantly from a linear or Couette profile, in being 'localised' near the walls ('Plug-Slip' or PS) or in the middle of the gap, which we call 'Central Localisation' (CL), for which there is experimental evidence [6]. The friction coefficient can be extremely low ( $\sim 0.01$ ) in the PS region as a result of incommensurate alignment between a (100) face-centered cubic wall plane and reconstructed (111) layers of the confined region near the wall. It is possible to exploit hysteresis to retain low friction PS states well into the CL high wall speed region of the phase diagram. Stick-Slip behavior due to periodic in-plane melting of layers in the confined region and subsequent annealing is observed at low wall speeds and moderate external loads.

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## Snap evaporation of droplets on smooth topographies

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Stick-slip evaporation is a widely used model to explain the evaporation of sessile droplets. During stick-slip evaporation, the shape of the droplet it has is subject to pinning and de-pinning of its edge from the solid surface. Surface pinning is attributed to either chemical or topographical defects on the solid. [1] Therefore, predicting and controlling the shape and position of a droplet during the process of evaporation is a major challenge. [2, 3, 4]

Recently, it has been shown that by replacing a dry solid surface by a flat liquid-infused surfaces (LIS), the edge of an evaporating droplet can be exempted from pinning. [5]

In this work, we show how on a non-flat LIS an evaporating droplet undergoes a predictable kinematics, where the droplet's shape undergoes a series of sudden reconfigurations which we call snap events. We focus on macroscopic droplets, up to 1 mm in size, for which the timescale of evaporation is much larger than its relaxation to the local mechanical equilibrium. Such a quasi-static situation holds for most of the evaporation process. Nonetheless, using a local stability analysis and lattice-Boltzmann simulations, we show that the stability or even the existence of equilibrium states can be lost as the droplet volume varies, thus causing a snap to a new quasi-static shape.

Unlike stick-slip evaporation, during snap evaporation the position of droplets can be controlled by topography. This can be exploited in the design of pinning-free surfaces for purposes of heat and mass transfer by evaporation.

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## Curvature effects for multicomponent droplets

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The surface tension of a planar liquid–vapor interface for an  $n$ -component mixture can be calculated when the  $n$  intensive thermodynamic variables for the coexistence state are given; for a pure component this amounts to specifying a point on the boiling point curve. For curved surfaces, such as those of droplets in equilibrium with a surrounding vapor, the thermodynamic state variables do not lie on the classical  $n$ -dimensional coexistence locus, and in fact  $n + 1$  variables are needed. This extra parameter can be chosen as the radius of the droplet, and it is highly interesting to know how surface tension and other properties depend on this radius. The curvature dependence can be expressed in terms of the total and Gaussian curvatures, and can for a single-component system be formulated to second order by the Helfrich expansion [1].

In the Helfrich expansion the main quantities of interest is the well-studied Tolman length [2], which is the first-order curvature correction compared to that of a plane surface, and the rigidity constants, representing the second-order corrections. For pure water, incorporating curvature dependence of surface tension can improve the nucleation rates predicted by classical nucleation theory [3]. However there are other important phenomena, such as the formation of oil-water emulsions, where the curvature dependence of the surface tension for a *multicomponent* droplet may become relevant. But so far, curvature effects for multicomponent droplets have been given little attention in the literature.

This work studies the curvature dependence of surface tension for multicomponent droplets. We discuss the Helfrich expansion appropriate for multicomponent droplets introduced in [1], which is independent of any model for the density profiles. We then introduce a specific density functional theory, namely the square gradient theory [4, 5], and present a route to calculate the coefficients in the curvature expansion. Finally, we give some attention to the thermodynamic stability of the resulting stationary density profiles.

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## Density functional theory for fluid-solid and solid-solid phase transitions

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We develop a theory to describe solid - solid phase transition. The density functional formalism of classical statistical mechanics is used to find exact expression for difference in the grand thermodynamic potentials of the two co-existing phases. The expression involves both the symmetry conserving and the symmetry broken parts of the direct pair correlation function. The theory is used to calculate phase diagram of systems of soft spheres interacting via the inverse power potentials  $u(r) = \epsilon (\sigma/r)^n$  where parameter  $n$  measures softness of the potential. We find that for  $1/n < 0.154$ , systems freeze into the face centred cubic (fcc) structure while for  $1/n \geq 0.154$  the body-centred-cubic (bcc) structure is preferred. The bcc structure transforms into the fcc structure on increasing the density. The calculated phase diagram is in good agreement with the one found from molecular simulations.



## Rheology of Confined Water using a Novel Rheometer

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The flow of water confined to nanometer-sized pores is central to a wide range of subjects from biology to nanofluidic devices. Despite its importance, a clear picture about nanoscale fluid dynamics is yet to emerge. Water permeation through hydrophobic channels, such as nanotubes, is five orders larger than expected from conventional fluid theory[1]. On the other hand, the measured viscosity through hydrophilic nanochannels is 30 percent larger than bulk water[2]. The viscosity measurement of nanoconfined water by independent means, such as Atomic force Microscopy (AFM) and Surface Force apparatus (SFA) have resulted in contradictory findings.

In this poster, I will present our efforts on measuring transport properties of confined water using a home-built small-amplitude AFM[3] and shear rheology using tuning fork based rheometer developed in our lab[4, 5]. Our new method is able to measure rheological response of liquids confined to nano-scale which exhibit a considerable slow-down in dynamics compared to bulk liquids[4]. The measurement showed a clear indication that the water under confinement exhibits viscoelasticity and shear thinning[5]. Recently, we measured dissipation in less than 25 nm thick water films and it was found to decrease for both wetting and non-wetting confining surfaces. The fitting of Carreau-Yasuda model of shear thinning to our measurements confirms again that the flow is non-Newtonian and for wetting surfaces the no-slip boundary condition is valid. On the contrary, for nonwetting surfaces boundary slippage occurs with slip lengths of the order of few nm. The findings suggest that both, the wettability of the confining surfaces and nonlinear rheological response of water molecules under nano-confinement play a dominant role in transport properties[6]. Using a recently developed instrument, which allows optical access to the confined region we are able to measure diffusion in water under confinement using Fluorescence Correlation Spectroscopy. This will allow us to perform microrheology to measure non-Newtonian response by independent means [7].

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## **Topic 8**

# **Supercooled Liquids, Glasses, Gels**

## Higher-order correlations in glass- and crystal-forming complex liquids

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Although glasses are very common in everyday life, the glass transition is one of the mysteries in condensed matter physics. Upon approaching this transition, the sample dynamics slows down by orders of magnitude while the static structure remains almost unchanged. In addition, relaxation phenomena become non-exponential pointing to a broad distribution of relaxation times and the existence of dynamical heterogeneities, suggested to be closely connected to spatial heterogeneities. In this contribution we will discuss the role of higher-order correlation functions for the glass transition of complex liquids from coherent X-ray scattering experiments.

First, we will present a microrheology study on the dynamics of polypropylene-glycol by means of X-ray photon correlation spectroscopy (XPCS) at temperatures ranging from room temperature to the glass transition temperature  $T_g$  [1]. Beside a cross-over from Brownian motion to hyperdiffusive and ballistic dynamics, dynamical heterogeneities increase dramatically upon cooling. This leads to two effects: (a) increasing spatial heterogeneity and (b) correlated motion at temperatures close to and below  $1.12 T_g$ .

Second, we will discuss structural higher-order correlations in colloidal systems by means of X-ray cross correlation analysis (XCCA) [2,3]. For hard sphere systems, we demonstrate the impact of such correlations on accessing the sample structure beyond pair-correlations [4]. In the vicinity of the hard-sphere glass transition, we observe (1) appearance of ordered clusters prior to the glass transition and crystallisation and (2) increasing medium-range order in colloidal glasses. Both observations are accompanied by a slowing down of the relaxation time, proving for the first time experimentally the relation of order formation and dynamics in a soft matter system [5].

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## Low and high density liquid structures in the polarizable BK3 model of water

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Water is known to exhibit a remarkably rich phase diagram. Despite of all the effort invested into research of water and molecular basis of its unusual properties, some of the phenomena remain at the level of

speculation. One of these is the hypothesis of the liquid-liquid phase transition and existence of the second critical point. This hypothesis can explain the anomalous behavior of water over a wide range of thermodynamic conditions but to date there has been no its confirmed verification. Computer simulations can cast light on this problem but they are intermolecular interaction model dependent and the results may thus be even controversial; some classical models reveal the coexistence of two liquids while other do not show such behavior.

To detect structural changes that take place in supercooled water with changes of the thermodynamic conditions, a number of parameters have been introduced with a common idea, in general, to quantify deviations from tetrahedrality. However, all these (and other) parameters suffer from various ambiguities, e.g., in setting a certain cutoff distance or specification of the extent of hydrogen bonding.

We have recently developed a new and general method, based on the Delaunay triangulation, for the identification of molecules forming the border between regions of an arbitrary shape, being it either different phases or any other molecular structures. We have performed extensive simulations on the polarizable BK3 model of water both in the supercooled region and at ambient conditions, and at supercritical conditions, and applied this method, along with the spatial distribution function (SDF), to analyze the structure. It appears that a number of geometrical functions characterizing the domains may exhibit bimodal distribution pointing to existence of two different structures in the system. More detailed insight is then provided by the SDF and a cluster analysis. These results have also been confirmed by the local structure factor showing the prevailing occurrence of the high density domain at ambient conditions and gradually increasing domains of low density when decreasing temperature along the isobar  $P=1$  bar. These results will be presented and discussed in details along with an overall picture of the behavior of supercooled water.

## TOApy program for investigation of the phase transitions

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Thermooptical analysis (TOA) of texture obtained from the polarizing microscope observation (POM) is a powerful tool for detection of phase transitions, especially in case of second-order transitions. We developed TOApy software, which allows for automatical transformation of the series of microscopy images to TOA plot showing light intensity vs. temperature. Thanks to TOApy program, TOA can be performed without photo diode, multicontroler etc. basing only on movie data obtained from POM even when changes of image details at phase transition are very weak. In the program discussed, three algorithms: gray, svd and rgb are used. During the polymorphism studies of 4-bromobenzylidene-4'alkyloxyaniline (5BBAA) compound TOA method allows for detection of vitrification ( $\text{Cr} \rightarrow \text{gCr}$ ) of conformationally disordered crystal not traced with help of DSC method [1].

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## Shrinking water's no man's land in the intermediate pressure regime

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One of the peculiarities that make water such a fascinating substance to study is the abundance of solid phases it can form. Due to its polymorphic properties as many as 17 distinct crystalline phases were described scientifically thus far, with more expected to be discovered. Also in the disordered solid state water exhibits this unusual diversity: three different amorphous solid phases have been distinguished, labelled by their variation in density – low-density amorphous ice (LDA), high-density amorphous ice (HDA) and very high-density amorphous ice (VHDA). As to the true nature of these phases and their distinctness from each other there has been much debate in the past decades. Least explored of these phases, and the most recent to have been described is VHDA.

This work is focussed on the examination of VHDA's crystallisation behaviour in the intermediate-pressure regime (0.70 - 1.80 GPa), i.e. crystallisation temperature and phase composition of the yielded crystalline phase / phase mixture. By examining the volume curves in situ in dependence of the temperature it is possible to extract onset and offset temperatures of crystallisation. Further ex-situ powder X-ray diffraction yields information on the obtained crystalline phase/phases. Various heating rates have been applied to study the kinetics involved. In comparison to results formerly obtained for unannealed high-density amorphous ice (uHDA)<sup>1</sup> it shows that especially at lower pressures VHDA exhibits a considerably higher thermal stability against crystallisation as uHDA (up to 16 K, dependent from the heating rate). Also, the process of parallel crystallisation (transformation into more than one crystalline phase upon crystallisation) is much more suppressed in VHDA than in uHDA. Thus, nanocrystalline seeds in the uHDA matrix - which have been reasoned to be the cause for lower thermal stability and less homogeneous transformation behaviour at lower pressures (0.1 - 0.5 GPa) when comparing uHDA to expanded high-density amorphous ice (eHDA)<sup>2,3</sup> - appear to be largely absent in the case of VHDA.

Furthermore, it appears to make a difference at which pressure VHDA is produced from uHDA (1.10, 1.60 or 1.90 GPa). The higher the pressure and annealing temperature (of formation from uHDA), the more thermally stable VHDA becomes against crystallisation when being heated isobarically at a given pressure.

The results suggest that VHDA produced at 1.90 GPa is the most equilibrated amorphous phase at elevated pressures  $p > 0.7$  GPa.

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# Integral equation theories, configurational overlap, effective potential and the Random First Order Glass Transition.

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We consider two weakly coupled replica of a dense system of  $N$  atoms interacting via a repulsive inverse-power potential, and calculate the mean value of the configurational overlap  $Q$  of the two replica as well as its mean-square fluctuation, using the hypernetted chain (HNC) and the self-consistent Rogers-Young (RY) closures of the integral equations for the pair structure of this symmetric "binary mixture". The Helmholtz free energy per particle  $f(\epsilon_{12})$  and its Legendre transform or effective potential  $W(Q)$  [1] are determined as functions of the thermodynamic parameters and the inter-replica coupling  $\epsilon_{12}$  or its conjugate variable  $Q$ . Analysis of the  $\epsilon_{12}(Q)$  and  $W(Q)$  curves shows that the two-replica system undergoes a transition between weak overlap and high overlap states below a critical temperature. The minima of  $W(Q)$  correspond to a supercooled liquid (L) and a glass phase ( $G_2$ ), while the intermediate maximum is associated with a thermodynamically unstable branch of solutions,  $G_1$  predicted in our earlier work [2]. The transition associated with a discontinuity of the mean overlap  $\langle Q \rangle$  order parameter [1, 3, 4, 5] may be considered as a precursor to the ideal (or "random first order" (RFO)) glass transition between the L and  $G_2$  phases. The RFO transition is characterized by the vanishing of the configurational entropy [1, 3, 4, 5] and by a weak discontinuity of the molar volume, implying that the ideal glass transition is a weakly first-order thermodynamic phase transition which requires an infinitely long equilibration time. Results obtained through the Rogers-Young (RY) closure confirm the qualitative predictions of HNC results, but with quantitative differences. Similarities and differences between integral equation approach and mean-field theory are discussed.

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## Effect of temperature jump on physical aging of gelatin gels

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Gelatin gels show slow structural and rheological evolution at temperatures below the gel point (physical aging) [1-3]. In this study, the aging dynamics and the effect of temperature jump during the aging on the structure and rheology of gelatin gels were investigated by small-angle X-ray scattering (SAXS), synchrotron vacuum-ultraviolet circular dichroism (VUVCD) or optical rotation (OR), and viscoelasticity.

In the isothermal experiments, SAXS results indicated the growth of the collagen helical structure as junction zones during the aging. The plots of storage modulus ( $G'$ ) versus helix amount ( $\chi$ ), obtained from viscoelasticity and VUVCD/OR, respectively, at different temperatures coincided with each other to form a master curve.

Two temperature jump protocols were examined: Protocol I ( $60^{\circ}\text{C} \rightarrow 5.0^{\circ}\text{C} \rightarrow 17.5^{\circ}\text{C}$ ) and Protocol II ( $60^{\circ}\text{C} \rightarrow 17.5^{\circ}\text{C} \rightarrow 5.0^{\circ}\text{C}$ ). The plot of  $G'$  versus  $\chi$  for Protocol I was on the master curve for the isothermal aging, but the plot of  $G'$  versus  $\chi$  for Protocol II deviated from the master curve. The melting curves of the gels for Protocol I and for the isothermal experiment coincided with each other, but the melting curve for Protocol II was different from that for the isothermal experiment, showing that the size distribution of the helical structure in the gelatin gels is sensitive to the thermal history.

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## Intimate link between crystallization and glass transition

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When a liquid is cooled below the melting point, it is either crystallized or vitrified depending upon the cooling rate. However, it is not clear what physical factors control the ease of crystallization, or the glass-forming ability. For hard and soft spheres, we found that crystal-like bond orientational order grows in both size and lifetime when the degree of supercooling is increased [1]. Furthermore, we revealed that such structural order plays a crucial role in crystal nucleation and polymorph selection [2-7]: In the early stage of crystal nucleation, the ordering proceeds with the enhancement of spatial coherence of crystal-like bond orientational order and is primarily 'not' driven by translational order. Translational ordering plays a crucial role only in the late stage. This indicates the importance of pre-ordering of a supercooled liquid, which takes place before crystal nucleation is initiated.

Extending this idea, we also show [8] that the degree of local structural ordering is a major controlling factor of the ease of crystallization (or, glass-forming ability): Stronger tendency of local crystal-like structural ordering leads to the lower energy barrier for crystal nucleation. In other words, the increase in the glass-forming ability is accompanied by the disappearance of crystal precursors in a supercooled liquid state, which mirrors the increased structural difference between liquid and crystal in the glass-forming region. More precisely, we reveal that the key parameter controlling the glass-forming ability is the interfacial energy scaled by the thermal energy. This may provide a general principle for the emergence of glassy behavior of a system with competing orderings, which we argue is valid whenever there is strong competition between two or more orderings,

Our study indicates that liquid-state theories at the two-body level may not be enough for the description of the phenomena taking place below the melting point and it is crucial to take into account many-body correlations [1,9].

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## Revealing the structural origin of dynamic heterogeneity in glass-forming liquids

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When a liquid is supercooled and approaches the glass transition, the drastic slowing down of its dynamics is accompanied by growing spatial heterogeneity. The origin of such slow dynamics and heterogeneity has been a long standing unsolved problem in condensed matter physics and material science. Here we introduce a new approach to reveal their structural origin, which may be valid for a wide class of glass-forming liquids. We find that the development of dynamic heterogeneity can be well predicted in the way of progressive spatial coarse-graining of an initial static structure: the mobility field gradually spreads from most disordered regions towards more ordered regions systematically following a relevant structural order parameter field, which captures many-body (orientational) correlations with a close link to local free energy. This clearly indicates that it is the static order parameter that controls dynamic heterogeneity. Furthermore, we reveal that the correlation between the static and dynamic field maximizes at a specific spatial coarse-graining length and time scale, which are respectively in accord with the dynamic correlation length and the structural relaxation time independently determined by traditional methods. This implies that the dynamical slowing down is a consequence of the growing static correlation length. We also find that the close correlation between the fast cage-rattling and slow glassy dynamics emerges as a natural result of their connections to the common static structure. Our findings strongly indicates a common static structural origin for the fast and slow dynamics of a supercooled liquid.

## The reversibility and first-order nature of liquid-liquid transition in a molecular liquid

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A liquid-liquid transition (LLT) is a transition between two liquid states, liquid 1 and 2, for a single-component substance [1, 2]. For molecular liquids, LLTs reported so far are all located in a supercooled liquid state metastable against crystallization. This intrinsically non-equilibrium nature of the transition has led to a number of serious debates concerning its origin: whether the transition is truly LLT or just a consequence of nano-crystal formation. So far most of experimental studies on LLTs in molecular liquids are on the transition from liquid 1 to a glassy state of liquid 2, glass 2, upon cooling, and there has so far been no convincing experimental evidence for the reverse LLT transition from liquid 2 to 1 upon heating, due to the interference by rapid crystallization. Here we report the first unambiguous confirmation of the reverse LLT from liquid 2 to liquid 1 following the glass 2-to-liquid 2 transition upon heating, by kinetically isolating the reverse LLT from the crystallization and the glass transition with an extremely high heating rate of flash differential scanning calorimetry and a special temperature protocol [3]. The results cannot be explained by the nano-crystal scenario, thus firmly establishing the LLT scenario. Furthermore, we reveal from the glass-transition behavior during the transformation that there exist nucleation-growth-type and spinodal-decomposition-type LLT. In particular, we confirm the coexistence of liquid 1 and 2 for the former, clearly indicating not only the first-order nature of the transition but also that the transition is indeed between two 'liquid' states. Our findings provide firm experimental evidence for the presence of LLT in a molecular liquid as well as its reversibility and first-order nature and shed new light on the very nature of the liquid state.

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## A transient amorphous solid formed from low density aqueous charged sphere suspensions

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Glass transition is one of the fundamental problems in condensed matter physics. Colloidal glasses are most commonly observed in hard spheres [1]. In charged sphere systems, they have so far been reported at elevated packing fractions, where strong self-screening renders the electrostatic repulsion very steep. Here we report the observation of a transient *low density* amorphous solid, formed in a thoroughly deionized suspension of highly charged latex spheres with diameter of 118 nm and moderate polydispersity. The transition occurs on the crystalline side of the freezing line for number densities of  $n > 2 \cdot 10^{-18} \text{ m}^{-3}$ . This corresponds to volume fractions of a few permille. The solids form within seconds to minutes. They display a liquid-like structure factor, a finite shear rigidity and a second, slow relaxation process [2]. Depending on the particle concentration, the samples transform to body centred cubic equilibrium crystals on time scales of hours at low and days at large number density. The location of the observed glasses in the effective temperature - density plane is consistent with recent expectations from mode coupling theory for hard core Yukawa particles. Although our data are still somewhat preliminary, this seems to be the first experimental observation of a low density Wigner glass formed from spherical colloids.

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## Dynamical instability causes the demise of a supercooled tetrahedral liquid

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In this work, we investigate the relaxation mechanism of a supercooled tetrahedral liquid (modeled by mW potential [1]) at its limit of stability using isothermal isobaric (NPT) Monte Carlo (MC) simulations. In similarity with systems which are far from equilibrium but near the onset of jamming [2], we find that the relaxation is characterized by two time-scales: the decay of long-wavelength (slow) fluctuations of potential energy is controlled by the slope  $[\partial(G/N)/\partial\phi]$  of the Gibbs free energy ( $G$ ) at a unique value of per particle potential energy  $\phi = \phi_{\text{mid}}$ . The short-wavelength (fast) fluctuations are controlled by the bath temperature  $T$ . The relaxation of the supercooled liquid is initiated with a dynamical crossover after which the potential energy fluctuations are biased towards values progressively lesser than  $\phi_{\text{mid}}$ . The dynamical crossover leads to the change of time-scale, i.e., the decay of long-wavelength potential energy fluctuations (intermediate relaxation). Because of the condition  $[\partial^2(G/N)/\partial\phi^2 = 0]$  at  $\phi = \phi_{\text{mid}}$ , the slope  $[\partial(G/N)/\partial\phi]$  has a unique value and governs the intermediate stage of relaxation, which ends just after the crossover. In the subsequent stage, there is a relatively rapid crystallization due to lack of long-wavelength fluctuations and the instability at  $\phi_{\text{mid}}$ , i.e., the condition that  $G$  decreases as configurations with potential energies lower than  $\phi_{\text{mid}}$  are accessed. The dynamical crossover point and the associated change in the time-scale of fluctuations is found to be consistent with the previous studies [3,4].

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## Non-equilibrium self-assembly in cement hydration

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Perhaps surprisingly, soft matter processes at the nanoscale crucially determine macroscopic mechanic properties and long-term evolution of common materials such as cement. During cement hydration, the dynamic physico-chemical environment dictates the evolution of the effective nanoscopic building blocks and their effective interactions. Here we use Monte Carlo and Molecular Dynamics simulations to study a coarse-grained model of this complex process comprised of colloidal nanoparticles with effective short-range attraction and long-range repulsion [1]. We observe that the structure and symmetry of the growing clusters strongly depends on the time evolution of the effective interactions during the non-equilibrium assembly process and map out the “dynamic phase diagram”. The two distinct pathway towards the final dense structure are via **i)** the formation of finite size isotropic clusters and **ii)** the growth of elongated clusters and percolated gel-like structures. The unique strength of cement is attained only with a proper balance between the early-stage gel formation and the continuous densification of the material. Our results enable us to design optimal kinetic pathways and propose new routes of material optimization with important implications for reducing concrete carbon footprint. Moreover, the underlying mechanism of non-equilibrium self-assembly is likely governing several other processes in nature such as protein aggregation or biomineralization.

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# Cosolute partitioning and gel permeability in swell-collapse transitions of random tetra-functional hydrogels

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We study diffusion and absorption of cosolute particles in semi-flexible tetra-functional gel networks by means of extensive coarse-grained molecular dynamics simulations in isothermal-isobaric ensembles. The gel system consists of randomly formed tetra-functional network regions and also bulk regions where the cosolutes diffuse in both regions, enabling a quantitative study of partitioning and permeability. The partitioning is a measure of cosolutes absorption into the gel [1], and the permeability signifies degree of cosolutes penetration through the gel [2]. The gel undergoes a sharp swell-collapse transition in changing solvent quality [3] and network-cosolute interactions [4]. Large structural fluctuations of the gel are found around the transition points. Throughout a wide range of parameter space of the solvent quality and the cosolute coupling, a rich topology of the partitioning landscape exhibits several distinct structural gel states including collapsed states in good solvent condition, induced by the cosolutes in a cooperative manner. In addition, we compute the cosolutes diffusivity inside the gel, which is highly correlated to the gel structural transitions, and in conjugation with the partitioning we obtain the permeability. The permeability turns out to be a drastic nonmonotonic function in the parameter space. We discuss how does the permeability differ from that in regular non-random network gels. We also present a theory that interprets our simulation results in terms of a virial expansion of the excess chemical potential and the excess entropy.

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## Nano-particle resolved studies of deeply supercooled liquids

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The physics underlying the glass transition is a major outstanding problem in condensed matter. Central to resolving this problem is whether there is some kind of thermodynamic glass transition or whether the massive slowdown of 14 decades in relaxation time is a dynamic phenomenon [1]. Among the key pieces of evidence in support of a thermodynamic phase transition would be concurrent growing dynamic and structural lengthscales, but measuring such quantities requires particle-resolved studies of colloids and simulations which have hitherto been unable to access states more deeply supercooled than the mode-coupling transition (4-5 decades of dynamic slowing). Crucially, at deeper supercoolings, theories such as random first order transition theory predict a different mechanism of relaxation [1], underlining the importance of studying deep supercooling.

Using super-resolution microscopy, we present results on 250 nm radius nanoparticles which are much smaller than any previously studied, and access deeper supercoolings than ever before for particle resolved studies. Unlike previous results at weaker supercooling [2,3], we find that a significant number of particles persist in icosahedral locally favoured structures (LFS), and that these structures display slow dynamics, exhibit a growing static lengthscale with density and are present in regions of high static overlap [4]. These findings may help to resolve the glass transition – in favour of an underlying thermodynamic transition [5].

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## Combined Cononsolvency and Temperature Effects on PNIPAM Microgels in Bulk Phase and at Interfaces

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Poly(N-isopropylacrylamide) (PNIPAM) based microgels are well known for their temperature dependent swelling in water. They exhibit a Volume Phase Transition Temperature (VPTT) of about 32°C above which they shrink because of the breaking of hydrogen bonds between water and polymer that are responsible for the swelling at lower temperatures. Shrinking can also be achieved by adding a cosolvent like ethanol. Ethanol itself is a good solvent for PNIPAM just like water, but microgels tend to shrink in the mixture of both. This is known as the cononsolvency effect and can be explained by the preferential adsorption of one of the solvents to the polymer.

The behaviour of microgels was studied in bulk using dynamic light scattering (DLS) and on wafers coated with a cationic polyelectrolyte (PAH) using atomic force microscopy (AFM). Volume minima have been observed at lower ethanol contents in bulk than on PAH surfaces[1]. Measurements of the VPTT indicate a decrease of the VPTT up to 30 vol% Ethanol. Beyond 30 vol% the VPTT disappears. In accordance with the difference between minima observed in Ref. [1], the VPTT is less significantly reduced for microgels spincoated from a water solution onto a PAH wafer than in bulk. However, changing the surface by using a gold coated wafer instead or varying the spincoating conditions leads to a behaviour on surfaces which is comparable to that in bulk. This effect is probably of microscopic origin, and is assumed to be caused by the structuring of the microgels and interdigitation with the PAH surface during the spincoating process.

In contrast to the well-known collapse beyond the VPTT in water, microgels in mixtures of water and ethanol are reswelling (to a lower extend) at high temperatures above 50°C in bulk. This behaviour corresponds to an upper critical solution temperature (UCST, microgel swells upon temperature increase). This is in agreement with the results of molecular dynamics (MD) simulations. They have shown that a delicate interplay between bulk solution properties and reduced preferential binding is responsible for the reswelling.

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## Fatigue in colloidal gels

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Solids weaken upon exposure to repeated stresses that are smaller than their yield stress. This process is known as fatigue. Fatigue is a complex process that results in sub-critical damage in a wide variety of materials. This damage manifests at the microscopic scale and is thus often invisible until it triggers the catastrophic failure of the material as a whole. Thus, understanding the microscopic origins of fatigue, which pre-empt macroscopic failure, is crucial to understanding the lifetime of materials.

Here we use colloidal gels as a model for heterogeneous solids. Colloidal gels are non-equilibrium networks of attractive colloids. The mechanical response of a colloidal gel is governed by a number of mesoscopic strands which together form a mechanically stable, percolating network. As gel strands are many particles wide, they do not directly rupture when a single bond breaking event takes place. The overall integrity of a gel strand is maintained by adjacent bonds and due to thermal fluctuations inter-particle bonds reform [1,2].

By combining Brownian Dynamics simulations and non-linear rheology we are able to separate the different processes underlying fatigue. Fatigue in colloidal gels is similar compared to biomaterials as fibrin and collagen in respect that the overall network structure is mainly conserved and individual strands are lengthened [3]. Additionally, microscopic mechanisms such as local necking are shown to play an important role in the weakening of the material.

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## Percolation threshold in the gelation process of DNA self-assembled structures

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The proper design of DNA sequences allows for the formation of well defined supramolecular units with controlled interactions *via* a consecution of self-assembling processes. This methodology has permitted the design of tetravalent nanostars (NS) with controlled valence,  $f$ , ruled by the presence of complementary single-strand overhangs placed at the end of each DNA NS arm, the so-called sticky-ends [1]. The performance of these patchy-systems is strongly related to the number of patches present on particles' surfaces [2] that in consequence limits the maximum number of bonds that particles will be able to form.

In previous results, we discussed the formation of a kinetically arrested homogeneous DNA hydrogel at low-T [3], however, little is known about whether the sol-gel transition is mediated by the formation of a percolating network.

Recent Dynamic Light Scattering (DLS) measurements have shown that is possible to use DNA NS as a model-system to investigate in a controlled way the percolation transition and the cross-over from chemical to physical gelation, exploiting the steep temperature dependence of the DNA nucleotides interaction free-energy. We have experimentally realized a system composed by a mixture of DNA chains (B, with  $f=2$ ) and DNA NS ( $f=4$ ) in which the only relevant interaction is between particles with different valence, thanks to the proper design of the sticky-ends. It was observed that by tuning the NS/B ratio according to the theoretical models of Flory and Stockmayer, it is possible to bring the system at a well defined distance from percolation.

We studied the dynamical evolution of the NS-B system in a window of temperatures ranging from 10°C to 55°C. The results showed an Arrhenius dependence, suggesting that the relaxation time decays measured are effectively mediated by the temperature, which controls the lifetime of the NS-B bonds. The ratio of NS and B particles was fixed at 4 different values to reproduce gel, fluid, an intermediate state between gel and fluid, and percolation conditions, proposing that the formation of a percolating network constitutes the threshold for gelation in branched biopolymer systems. It will be discussed that close to the percolation point, Flory-Stockmayer theories suggest the formation of NS-B clusters composed of different amounts of NS and B structures. Therefore, the associated density autocorrelation functions are characterised by a typical decay time, which is directly related to the cluster size. The emergence of a logarithmic decay in the autocorrelation functions obtained out from these DLS experiments comes to validate these hypothesis.

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Thermodynamic and kinetic anomalies are often encountered in tetrahedral liquids, most famously in water (for example, the density anomaly), but also in SiO<sub>2</sub> and Si. The origin of the anomalies is often linked to behaviour of quantities associated to phase transition phenomena which occur in the metastable supercooled regime that is largely inaccessible by conventional experiments leaving simulations as a convenient alternative. Several theories and scenarios have been proposed that link behaviour of anomalous properties to the existence of a liquid-liquid critical point [1] but none can predict or explain the appearance of anomalies. Stillinger-Weber (SW) potentials are often employed to model tetrahedral liquids. These potentials are composed of a standard pairwise term with exponential decay and a triplet term which penalizes deviations from ideal tetrahedral angles[2]. In recent years the critical point for SW silicon has been uncovered [3] and loci of anomalous properties calculated for constant pressure for different strengths of triplet term in SW potential[4]. However, no systematic study of the SW potential that links the emergence of anomalies to topology of network has yet been reported. In this study we take a systematic approach to explore the parameter space of the triplet term in the SW potential at various temperatures, pressures and densities. This enables us to more thoroughly understand the appearance of thermodynamic anomalies in tetrahedral liquids and their connection to the network topology of the system. A possible connection between the existence of anomalies and crystal phases underlying the liquid is also explored.

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## Shape effects on the rheological behavior of polymer-grafted nanoparticles in solution

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The large majority of rheological investigations with soft colloids involve spherical particles. However, in several applications the particles are anisotropic. Here, we focus our attention on polymer-grafted nanoparticles in solution and compare three soft systems with the same chemistry, similar grafting density, same number of monomers per grafted arm but different core shape (spheres, cylinders and lamellas). Solutions in the dense regime at the same mass concentration have been investigated by means of light scattering and rheology in both linear and nonlinear regime. We find that, at the same weight concentration the shape affects substantially the relaxation times, yielding mechanisms and residual stresses, which reflect different particles arrangement in solution. We compare against relevant data in the literature with hard spheres, ellipsoids and other soft spheres, and attempt at extracting a generic phenomenological picture of rheology vs. shape and concentration.

## Static structure of densified GeSe<sub>2</sub> glass

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GeSe<sub>2</sub> and other Se-rich germanium selenide binary systems make network-forming glass easily. These materials have semiconducting properties attracting scientific interests for application to electronic devices. Focusing on GeSe<sub>2</sub>, its crystalline state consists of GeSe<sub>4</sub> tetrahedral units. In contrast with similar binary crystalline AX<sub>2</sub> type systems, e.g., SiO<sub>2</sub>, which consists of only corner-sharing SiO<sub>4</sub> tetrahedral units, there are not only corner-sharing GeSe<sub>4</sub> tetrahedral units but also edge-sharing GeSe<sub>4</sub> tetrahedral units, as a result, the crystalline GeSe<sub>2</sub> has a layered structure. In a GeSe<sub>2</sub> glassy state, three dimensional network is formed mainly consisting of corner-sharing tetrahedral units. Edge-sharing GeSe<sub>4</sub> tetrahedral units also exist in the glass GeSe<sub>2</sub>.

When AX<sub>2</sub> type compound is compressed, the crystalline structure of AX<sub>4</sub> tetrahedra transforms to denser crystalline state. In the case of SiO<sub>2</sub>, the  $\alpha$ -quartz transforms to coesite, and stishovite with increasing pressure. In the coesite SiO<sub>2</sub>, SiO<sub>4</sub> tetrahedral units still exist in spite of densification by compression. However, in the stishovite SiO<sub>2</sub>, the coordination number of Si-O changes from 4 to 6, i.e., SiO<sub>4</sub> tetrahedral units transform to SiO<sub>6</sub> octahedral units. In the glass SiO<sub>2</sub> state, the similar transition from tetrahedra to octahedra occurs above approximately 20 GPa. If the SiO<sub>2</sub> glass state compressed up to about 20 GPa is depressurized, its density recovers that of the ordinary SiO<sub>2</sub> glass at ambient pressure. By contrast, the density at ambient pressure becomes 20 % higher than that of the ordinary glass when depressurizing the glass state compressed above 20 GPa. This glass densified even at ambient conditions is known as the permanent densified glass.

On the other hand, focusing on the pressure-induced structural change of GeSe<sub>2</sub> glass, phase transition from tetrahedra to octahedra is also expected with compression. However, recently, Properzi *et al.* reported that complete geometry transforming from tetrahedra to octahedra does not occur yet until 30 GPa [1]. By depressurizing the glass state to ambient conditions, the permanent densification has been observed when the glass is compressed above a certain pressure [2]. However, such densification mechanism of glass GeSe<sub>2</sub> is still unclear.

We have investigated the static structure of densified GeSe<sub>2</sub> glass based on *ab initio* molecular dynamics simulations. The decompression process is started from 20 GPa at 300 K. In contrast to the ordinary glass, the number of fivefold-coordinated Ge atoms increases in the densified one. The peak position of three-body bond angle distribution for Se-Ge-Se of densified glass decreases from 109.47° to about 90°. Furthermore, the densification mechanism is investigated by the ring analysis, which is taking Ge-Ge and Se-Se homo-polar bonds into account based on the Mulliken populations analysis. The average ring size in densified glass is much smaller than that in ordinary glass.

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# Inhomogeneous local packing densities and bonding natures of melt-quenching $\text{Ni}_{67}\text{Zr}_{33}$ amorphous alloy

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Pulsed neutron diffraction and synchrotron X-ray diffraction measurements were performed on a melt-quenching  $\text{Ni}_{67}\text{Zr}_{33}$  amorphous alloy sample. A three-dimensional structural model was constructed by using reverse Monte Carlo (RMC) modelling method [1] with fitting to the neutron and x-ray diffraction data sets. The Voronoi-Delaunay method was used on the RMC configuration to investigate the local packing properties of each coordination cluster. With reference to the macroscopically averaged packing fraction, dense packing domains and loose packing ones were observed in the structure of  $\text{Ni}_{67}\text{Zr}_{33}$  amorphous alloy. The dense packing domains are formed by both the Ni- and Zr-centered clusters in almost equal proportion ( $\sim 52$  at.% Zr). On the other hand, the loose packing domains are mainly formed by Ni-centered clusters ( $\sim 12$  at.% Zr).

It is thought that the atomic arrangement of a melt-quenching amorphous alloy is affected by the presence of chemical short-range order in the liquid state. The thermodynamic properties of the liquid Ni-Zr system have been studied by several researchers.[2-5], and these results show that the mixing enthalpy curves show minima at around 37 at.% Zr [5] or more Zr-rich composition.[2] The strong chemical short-range order is present at around the composition in the liquid state. These thermodynamic evidences suggest that the dense packing domains in the structure of  $\text{Ni}_{67}\text{Zr}_{33}$  amorphous alloy, which consists of almost equimolar ratio, are thermodynamically stable.

The pair distribution functions show that the Ni-Zr nearest neighbor distances for the dense packing domains are shorter than those in loose packing ones. These results indicate that the dense packing domains are tightly packed through the strong heteropolar bonds.

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## X-ray cross-correlation of supercooled water via coherent x-ray scattering

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Understanding the structure of water in the supercooled regime ( $273\text{ K} > T > 232\text{ K}$ ) and in the no man's land ( $T < 232\text{ K}$ ) is one of the most fundamental questions in water research. A handful of challenging experiments on supercooled water by x-ray scattering and spectroscopy have provided valuable data on the atomic pair correlation functions via the measured structure factor ( $S(q)$ ) [1-4]. Beyond the typical structure factor information, x-ray cross-correlation analysis (XCCA), a technique using diffraction patterns from coherent x-ray scattering, has successfully enabled to extract details on the different local angular symmetries in a sample [5-7], e.g. a colloidal glass exhibited 4-, 5- and 6-fold symmetries at distinct lengthscales [5].

Here, we will describe our coherent x-ray scattering experiment [8] on supercooled water and results from the subsequent XCCA study on the measured and simulated diffraction patterns to understand the local order in supercooled water. We use a liquid jet system to obtain micrometer sized droplets in vacuum, which then cool rapidly due to evaporation reaching the supercooled regime, and impinge these droplets with ultrashort ( $\sim 100\text{ fs}$  at  $120\text{ Hz}$ ) coherent x-ray pulses at a Free-Electron Laser (FEL) source [8]. We will present our analysis efforts with the experimental data and also provide parallels to measurements with simulations of an ideal x-ray experiment with TIP4P/2005 water molecules, and the sensitivity of the different XCCA order parameters to the formation of ice nuclei in the simulations.

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# Gravity, Hydrodynamics and Fivefold Symmetry in Hard Sphere Nucleation Discrepancy

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Crystallisation is a long-standing challenge, due not least to its local nature, where rare events on microscopic time- and length-scales initiate the macroscopic phase transition [1,2]. Bridging these time- and length-scales is a formidable task, and one system has emerged as an ideal testing ground for a comparison of theory and experiment. This is the hard sphere model, prized for its simplicity, yet capturing the essential thermodynamics. Furthermore, systems very close to hard spheres can be realised with colloidal suspensions [3], which can be imaged at the particle level, provided an unprecedented opportunity to compare prediction and reality [4].

However, while good agreement between experiment and theory is found at high supersaturation, where crystallisation is rather rapid [2,5], at weaker supersaturation a wild discrepancy exceeding ten orders of magnitude emerges [2,6]. It is important to resolve this discrepancy, as the computational methods used to tackle these rare events - for example umbrella and forward flux sampling - are used in very many different applications, yet the hard sphere nucleation remains a rare example where prediction and experiment can be directly compared. It has been suggested that discrepancy may be related to sedimentation in the experiments (which is absent in the predictions) [7] and recently shown that the presence of fivefold symmetry in the metastable hard sphere fluid has a profound effect on the nucleation rate [8]. Here we combine these two concepts and show that the local structure hard sphere fluids indeed changes upon sedimentation. Using umbrella sampling which incorporates the changes in local structure, we find a significant drop in the nucleation barrier, such that the discrepancy between experiment and prediction is much reduced.

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## Formation and characterisation of tough protein gels

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Bigels are a specific class of double network gels that consist of two discrete but interpenetrating gel networks, producing a material with enhanced mechanical properties. Double network materials composed of both synthetic and natural materials have been described [1, 2]. By careful control of solution conditions, protein chemistry and kinetics, it is possible to form double network materials from two interpenetrating protein networks [3]. The inherent biocompatibility of the proteins provides advantages over synthetic materials for biological applications. We have characterised several different protein bigels using cavitation rheology and demonstrated that double networks with a range of elastic moduli can be formed. Depending on the bigel composition, deformation can be elastic, or fracture of the gel can occur. The tuneability of the material properties means that the protein double networks have a range of potential applications in drug delivery, wound healing and as biomimetics.

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## Complex disorder in binary mixtures: Analysis of the thermodynamic factor

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Molecular dynamics simulations were used to study binary mixtures which exhibit a specific structural organization. We distinguish complex disorder, defined by the presence of microheterogeneous spatial associations of molecules and simple disorder, which characterizes totally homogeneous mixtures. These structural properties are related to the behavior of the Kirkwood-Buff integrals (KBI). The KBI are defined as integrals of radial distribution functions and, as such can be obtained from computer simulations. Equally, they can be measured using thermodynamic properties, such as partial molar volumes, compressibility and partial derivative of the chemical potential with respect to concentration. The latter is called thermodynamic factor and is a quantity of a particular interest, since it is an indicator of the stability of a mixture with respect to mixing or demixing. Here we verify the reliability of the two different approaches: the calculation of thermodynamic factor from KBI and from the excess Gibbs free energy. We start with a simple system, two component Lennard-Jones mixture and advance to more realistic models, such as alcohol + benzene mixtures. The results show that the two methods qualitatively agree.

# Adiabatic Calorimetry Study of Surface-Induced Melting of Ice Confined in Controlled Porous Glass

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Surface-induced melting of ice [1] confined in controlled porous glass (CPG) with an average diameter of cylindrical pores of 500 angstrom [2] is studied by adiabatic calorimetry at the temperatures down to 225 K. We have found that a low-temperature excess of the apparent heat capacity of ice is associated with ice premelting contribution that grows on heating as an inverse power of deviation from the bulk ice melting temperature, with an exponent  $4/3$ . Under assumption of temperature-independent latent heat of ice melting, we concluded that low-temperatures surface-induced melting of water ice is controlled by the van der Waals interfacial repulsion resulting in a power-law divergence of the quasi-liquid layer thickness with an exponent  $1/3$  [3]. The latter contradicts the conclusions of paper [4] that are based on a high-energy x-ray reflection experiments.

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## Percolation of Patchy Colloids on Patterned Substrates

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Patchy colloids are functionalized colloidal particles with interacting sites on the surface. Increasing the colloidal concentration in a system of particles with valence higher than two drives a transition from a nonpercolated state, consisting of finite colloidal clusters, to a percolated state (or gel), where one of the clusters spans the entire system [1].

Here, we use Monte Carlo simulations to understand how the presence of a patterned substrate modifies the percolation transition in a system of patchy colloids in two dimensions. Two-dimensional systems of colloids often arise at interfaces or submonolayer adsorption on surfaces. We model the colloids as hard disks adsorbed on a substrate. The substrate is patterned with a periodic arrangement of identical attractive or repulsive wells of a predetermined size. For attractive wells we show that the substrate induces a uniform growth of the clusters at low colloidal concentrations and a semi-discretization of the cluster size distribution at high colloidal concentrations. The density at the percolation transition strongly depends on the size of the wells in a non-monotonic fashion. The percolation density increases (decreases) with respect to that in a uniform substrate for small (large) enough attractive potential wells. The case of repulsive wells features an unexpected region of well sizes for which an increase of the colloidal density results in reentrant percolation. A similar phenomenon has recently been found in patchy colloidal mixtures under gravity [2].

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## Glass Transition in Supercooled Liquids with Medium Range Crystalline Order

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If allowed to relax for astronomically long time at low temperatures, whether a glass forming liquid will start to form locally favored crystalline structures and eventually form a crystal is still actively researched with no clear consensus. Are the molecular mechanisms for glass transition in liquids with and without medium range crystalline order same? The question is important to answer because if the liquid eventually starts to form crystalline domains while approaching the glass transition then the complexity of the problem may simplify and may just be governed by the physics of the growing crystalline order. If not then there exists a new class of glass forming materials whose molecular mechanism for slowing down of dynamics will probably be easier to understand in terms of the dynamics of the growing medium range crystalline order. In this study we have performed extensive molecular dynamics simulations of few glass forming liquids in two dimensions and showed that the static and dynamics of glasses with medium range crystalline order are generically different from other glass forming liquids with no predominant local order. This study also resolves an important issue regarding the order agnostic nature of Point-to-set correlation function in correctly measuring the relevant length scale associated with dynamic slowing down.

## Common mechanism for the devitrification and ageing of hard sphere glasses

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Ageing and devitrification are very slow dynamical processes taking place in glasses. Both entail a slow evolution of the physical properties of a material, often to detrimental effect e.g. ice formation in cryogenic samples, volume change in high-precision applications, degradation of pharmaceuticals. The kinetic pathway by which such changes occur is far from fully understood, and has inspired numerous studies in recent years: in particular, Sanz *et al.* [1] showed that crystallization in a deeply supercooled hard sphere glass took place in intermittent steps accompanied by the large, collective motion of particles, or ‘avalanches’. Despite a detailed description of their phenomenology, the exact mechanism by which such events initiate, propagate, and cause structural change in the system remain unclear.

In this work, we carried out Brownian Dynamics simulations of WCA glasses at high effective volume fractions. We are able to catalogue a range of events in both devitrifying and ageing systems and distinguish avalanche initiators (AIs) from the cascade of particle motion (APs) that follows. We found that AIs are found in regions with particular structural characteristics, employing local Voronoi density and bond-orientational order as descriptive metrics. We also show that transient mechanical stability and the Maxwell stability criterion play important roles in the intermittent nature of the dynamics as well as propagation of APs, leading to a significant perturbation in an otherwise quiescent configuration that leads to structural evolution in other parts of the system. Both ageing and devitrification follow remarkably similar kinetic pathways, particularly when looking at the density field, despite differences in how their evolution couples with development in bond-orientational order.

It is hoped that the discovery of a common pathway through which ageing and crystallization destabilize a glassy state may lead to molecular design principles that might help engineer a more stable glass.

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## Simple scenario for glass transition phenomena based on liquid-liquid transition framework

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We propose a simple scenario for glass transition phenomena. There are two new aspects in it: (1) Liquid-liquid (*l-l*) transition with a critical point is assumed and the entropy accompanying it is discussed. (2) Time concept is introduced to this transition entropy.

In the traditional framework [1], the slow dynamics of glass forming liquids has attributed to supercooling and the configurational entropy has been discussed. But it propounds some critical problems including so-called Kauzmann paradox [2]. In our scenario, we seek the origin of the slow dynamics in critical fluctuations of *l-l* transition and discuss the transition entropy accompanying it. It enables us to avoid the Kauzmann paradox and to obtain a simple interpretation to the fragility index of glass forming liquids: It is a parameter indicating how close the pressure of the liquid to the critical pressure of *l-l* transition. This can explain the pressure dependence of the fragility observed in liquid glycerol [3] and is consistent with Angell's 'big picture' [4]. On the other hand, it has been concluded that the entropy effect accompanying *l-l* transition substantially slows down the ultrasonic sound velocity at MHz frequency [5]; however, our recent study [6] on liquid water and liquid Te mixtures (with Se or Ge) [7], which are expected to undergo *l-l* transition, revealed that the sound velocity at THz obtained by inelastic x-ray scattering measurements is insensitive to *l-l* transition. These results can be simply interpreted if we introduce time concept to this transition entropy: If the frequency is high enough compared to the inverse of the characteristic time of the system, the transition entropy is frozen. Similar concept has been discussed among theorists to overcome the broken ergodicity [8]. In this scenario, the abrupt change of the specific heat observed at the glass transition is no more than the time dependence of transition entropy. That is, the glass transition is not a thermodynamic phase transition at all, but is regarded as a part of *l-l* transition.

Our scenario can give many results with a simple manner as will be presented at the conference. We look forward to fruitful discussion with all of you.

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## Controlling fragility from strong to fragile using an isotropic short-ranged pairwise potential

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The fragility, which characterizes the temperature dependence of the transport properties, is one of the most important concepts of the glass transition. It is well known that anisotropic tetrahedral network-forming liquids such as silica ( $\text{SiO}_2$ ) glasses exhibit the Arrhenius behavior, while isotropic short-ranged potential liquids act as another type of glass former exhibiting super-Arrhenius temperature dependence. Here, it is demonstrated that the fragility can be controlled over a wide range by tuning the potential in a single simulation model. Our simulations are based on a silica glass former model originally proposed by Coslovich and Pastore (CP) [1]. This CP model uses the short-ranged and attractive pairwise potential between Si and O in order to mimic the anisotropic tetrahedral network structure. We reveal that the reduction of the potential depth, eventually transforming into the isotropic structure with the purely repulsive soft-sphere potential, seamlessly changes the temperature dependence of the relaxation time from Arrhenius to super-Arrhenius [2].

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## Mermin-Wagner fluctuations in 2D amorphous solids

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In a recent commentary, Mike Kosterlitz described how David Thouless and he got motivated to investigate melting and suprafluidity in two dimensions [1]. It was due to the lack of broken translational symmetry in two dimensions - doubting the existence of long range magnetism and crystals in 2D - and the first computer simulations foretelling 2D crystals (at least in tiny systems). The lack of broken symmetries, proposed by David Mermin and Herbert Wagner, is caused by long wavelength order-parameter fluctuations [2, 3, 4]. Those fluctuations do not only have structural impact but additionally a dynamical one: They cause the Lindemann criterion to fail in a 2D crystal in the sense that the mean squared displacement of atoms is not limited.

Differences between the 2D and 3D glass transition were recently reported in computer simulations [5]. Taking Mermin-Wagner fluctuations into account those differences can be explained naturally [6]. Comparing experimental data from 3D and 2D amorphous solids with 2D crystals, we disentangle Mermin-Wagner fluctuations from glassy structural relaxations [7]. The results are consistent with the work of Vivek et al. who investigated 2D and 3D glasses with short and long range particle interaction [8]. Very recently Hayato Shiba and coworkers verified Mermin-Wagner fluctuations in large scale computer simulations using an alternative approach [9]: The density of vibrational states of a 2D amorphous solid shows an infinite growth of acoustic vibrations, very similar to 2D crystals. Furthermore, the fingerprint of Mermin-Wagner fluctuations, namely the logarithmic increase of displacements with system size, was now demonstrated in 2D glass [9, 7] - fifty years after the prediction in symmetry breaking systems: crystallinity is not a requirement for Mermin-Wagner fluctuations which conserve the homogeneity of space and soften 2D ensembles in the thermodynamic limit.

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# Connectivity, Dynamics, and Structure in a Tetrahedral Network Liquid

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Liquids with tetrahedral structure are ubiquitous in nature. Some archetypal examples are liquid water, silica, or silicon. Despite presenting a great interest in fundamental science, the connection between microscopic dynamics and structure is still unclear in these systems. In particular, one of the most distinctive features of the equilibrium relaxation in these and other disordered systems, whose understanding is still elusive, is the emergence of microscopic cooperative motion at low temperatures [1].

In this work we report a comprehensive computational study on the interplay between connectivity, dynamics, and structure in a liquid of patchy particles [2] which develops an amorphous tetrahedral network upon decreasing temperature [3]. By means of a novel methodology, we investigate the system connectivity by discriminating the particles into different populations according to their number of bonds and show how the particle bonding process is not randomly independent but it manifests clear bond correlations at low temperatures as a result of the particle bonding cooperativity. We further explore the dynamics of the system and establish a clear relation between particle mobility and particle connectivity. In particular, we provide evidence of the so-called *anomalous yet Brownian diffusion*, a non-Gaussian diffusive behavior that has recently aroused interest due to its manifestation in biological, colloidal, and socio-economical systems [4]. Finally we widely investigate the dynamics and structure of the system in Fourier space and identify two quantitatively similar length scales, one dynamic and the other one static, which increase upon cooling the system and suggest a link between structure and dynamics at large spatial scales. We summarize our findings in an appealing qualitative picture where the low-temperature liquid is understood in terms of an evolving network of metastable cooperative domains of particles [3].

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## Identification of time-scales that support violation or preservation of Stokes-Einstein relation in supercooled water

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The Stokes–Einstein (SE) relationship between the shear viscosity and the translational diffusion constant of liquids is an important characteristic of their transport properties. The SE relationship breaks down in the case of glassy states. In fact, such violation of the SE relationship is “generally” observed in supercooled liquids. However, the physical origin of this SE violation remains elusive. In particular, for supercooled water, the SE violation coincides with other significant unsolved problems such as fragile-to-strong crossover in transport properties and liquid-liquid transition between a high- and a low-density liquid. Therefore, clarification of the physical implications of the SE violation is very important for achieving a deeper understanding of the aforementioned unsolved problems. Unfortunately, the high computational costs of the calculation of the shear viscosity have prevented a thorough investigation of the SE violation in supercooled liquid water to date.

In our study, we describe a systematic investigation of the SE relationship in supercooled liquid water [1]. We present the results of molecular dynamics simulations over a wide temperature range, including comprehensive numerical calculations of the shear viscosity using the shear stress correlation function. In particular, the role of the time-scales associated with various dynamical properties including hydrogen-bond (HB) breakage on the SE relationship is discussed. Most importantly, we found that the SE relationship is violated when the structural relaxation time is utilized; however the SE relation holds, even for supercooled states, when the HB lifetime is used. That is, the appropriate time scale supporting the SE relationship is surprisingly determined by the HB network rearrangement processes. This SE preservation was revealed to be due to the activated jumping of mobile water molecules during the HB breakages, which characterizes the diffusion constant. We have revealed that local rearrangements are directly connected with those jumping motions in other glass forming liquids such as soft-sphere mixtures (fragile liquids)[2] and silica-like network-forming liquids (strong liquids)[3]. Thus, our comprehensive results suggest that the SE violation observed in various glassy systems can be completely resolved through a unified description of local rearrangement events that cause the activated jump motions to exceed an energy barrier between local metabasins.

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## Potential Energy Landscape of the TIP4P/2005 model and the water anomalies

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Despite its simple molecular structure, water is an example of a complex liquid. Especially its low-temperature behavior in the super-cooled regime is still puzzling. We try to shed some light on the properties of super-cooled water by investigating the most accurate classical water potential available today, namely TIP4P/2005. Within the potential energy landscape framework, we try to verify the landscape properties responsible for the anomalous thermodynamic behavior. Therefore we study which areas of the landscape are sampled at a given temperature and density by determining the inherent structures (local potential energy minima), i.e., configurational properties, and the associated vibrational degrees of freedom. This allows drawing conclusions on the configurational properties of super-cooled TIP4P/2005 and its liquid-liquid critical point.

## Coordination number statistics of cluster formation in 2D colloid-polymer mixtures

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Understanding the formation, ageing and failure of particle gels is both of fundamental interest and industrial importance. Numerous commercial products contain active ingredients which fall within the boundaries of the colloidal domain. Polymers or clays, are routinely added to these systems as thickening agents. The addition of which often results in the formation of particle or colloidal gels, the lifetime and behaviour of which can be difficult to predict.

By studying the formation of such systems, insight can be gained into their behaviour and evolution with the passing of time. Two key pathways have been identified as potential routes to kinetically arrested particle gel systems. Phase separation via spinodal decomposition and equilibrium gels without phase separation can both result in percolating particle gel networks [1]. It has also been reported that cluster formation is an important consideration during these dynamical arrests [2], though the exact underlying mechanism by which arrest occurs is still not completely understood.

Here we probe diffusion limited cluster formation in a two-dimensional (2D) colloid-polymer mixture. In particular, we analyse the cluster formation using coordination number statistics and simple probability theory [3]. An explicit link between particle coordination number and mean cluster size is derived. Experimental results are compared to that of a theoretical model, based on a closed-packed cluster geometry, which grows by the sequential addition of close-packed shells. We find that our experimentally observed coordination number statistics during cluster formation is surprisingly well-described by the growth as predicted by our simple model.

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## Releasing frustration for better relaxation

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Among the most enduring pictures of dynamic arrest is that liquids form geometric motifs upon supercooling. In Euclidean space, such system-specific motifs are incompatible with a crystalline structure and give rise to a frustrated, slow dynamics. However, it is possible (at least in computer simulations) to promote the growth of locally ordered regions based on the preferred geometric motifs in two ways: i) slightly modifying the composition of the liquids [1] or ii) slightly perturbing the curvature of the space the liquids are embedded in [2].

We explore these two routes to control frustration in two atomistic models of glass formers and find that slow dynamics is very robust to both the two kinds of perturbations. In particular, we find that while for weak frustration the collective behaviour of the system is dominated by the presence of geometric motifs, for large frustration the dynamical slowing down occurs on scales much larger than the extent of the geometric domains, suggesting that additional mechanisms come into play.

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## Shear Thinning in Glassy Liquids

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Shear thinning is one of the most ubiquitous non-Newtonian rheological responses in soft matter. For glassy materials, the underlying mechanism behind the shear-thinning behavior still remains unclear. In almost all existing simulations and experiments, shear thinning is found to occur at a shear rate several orders of magnitude smaller than  $1/\tau_\alpha$  [?], where  $\tau_\alpha$  is the structural relaxation time. This fact is important because it implies that the usual constitutive instability is not relevant in explaining shear thinning in glassy liquids. In this study, aiming at elucidating this key rheological feature, we propose a simple theoretical model for describing the onset of shear-thinning in a high density glassy liquid. In a shear flow, along the compression axis, the overlap between neighboring particles is more enhanced than that at equilibrium, meaning that the “effective” size is reduced along this axis. On the other hand, along the extension axis perpendicular to the compression axis, the average structural configurations are stretched, but it does not indicate the expansion of the “effective” size itself. This asymmetric shear flow effect for particles results in a small reduction of the “effective” density. Because, in glass-forming liquids, the structural relaxation time strongly depends on the density,  $\rho$ , even a very small reduction of the effective density should lead to a significant decrease of the relaxation time under shear flow. We predict that the crossover shear rate from Newtonian to non-Newtonian flow behaviors is given by

$$\dot{\gamma}_c = \left[ \rho \left( \frac{\partial \tau_\alpha}{\partial \rho} \right) \right]^{-1}, \quad (1)$$

which can be much smaller than  $1/\tau_\alpha$  near the glass transition point. It is shown that this prediction is consistent with the results of molecular dynamics simulations. Furthermore, this criterion is expressed only in terms of experimental observables and should thus be useful in designing the processing of glass-forming liquids and metals.

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Freezing of liquids are well known by laymen and are fundamental for many areas of the sciences. We present a theoretical framework [1] for the thermodynamics of freezing. Properties of the crystal and liquid at a single state-point allow one to predict the coexistence pressure as a function of melting temperature, as well as the variation along the melting/freezing lines of quantities such as the reduced crystalline vibrational mean-square displacement (the Lindemann ratio), the liquid diffusion constant or the viscosity. The fundamental assumption is hidden scale-invariance of liquid and crystalline states [2, 3]. An analytical expression is available for systems of particles interacting via pair potentials that are differences of two inverse power laws. The theory is validated by computer simulations of the freezing and melting properties [4] of the 6-12 Lennard-Jones system. Finally we will outline an extension of the theory to crystallization in the super-cooled regime.

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## Yield in Amorphous Solids: The Ant in the Energy Landscape Labyrinth

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It has recently been shown that yield in amorphous solids under oscillatory shear is a dynamical transition from asymptotically periodic to asymptotically chaotic, diffusive dynamics. However, an understanding of the physics of this transition is lacking. Here we show that the diffusive behavior of the vector of coordinates of the particles comprising an amorphous solid when subject to oscillatory shear, is analogous to that of a particle diffusing in a percolating lattice, the so-called “ant in the labyrinth” problem, and that yield corresponds to a percolation transition in the lattice. We explain this as a transition in the connectivity of the energy landscape, which affects the phase-space regions accessible to the coordinate vector for a given maximal strain amplitude. This transition provides a natural explanation to the observed limit-cycles, periods larger than one and diverging time-scales at yield. [1]

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## Selectivity of reactants through a thermoresponsive hydrogel

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Thermoresponsive hydrogels, such as Poly(N-isopropylacrylamide) (PNIPAM), are recently becoming very popular as ‘smart’ carriers in modern nanoscience. For a large range of developments, *e.g.*, for drug delivery or nanocatalytic carrier systems, the selective adsorption and partitioning of molecules (ligands or reactants) inside the polymeric matrix are key processes that have to be controlled and tuned for the desired material function. The PNIPAM hydrogel structure undergoes a transition from a swollen into collapsed state upon raising the temperature, which alters the selectivity for diffusing particles. Catalytic model reactions based on nitrobenzene derivatives nicely demonstrate such a selectivity [1], where the reaction rates dramatically change after the transition. In order to gain insights into the nanoscale structure and binding details in such systems, we employ molecular dynamics simulations of a PNIPAM hydrogel in explicit water in its swollen as well as in a collapsed state [2]. We study various representative reactant types with a focus on aromatic solutes. We find that the adsorption generally raises with the size of a solute, whereas the temperature-dependent affinity to the chains is highly solute specific. The selectivity of reactants depends on the diffusion as well as the solvation properties of reactants in the hydrogel. While the swollen state gives rise to higher diffusivity, the collapsed state of the hydrogel increases the absorption ability of most of the reactants, leading to their higher enrichment. The competition between both is the key determinant for a total selectivity and permeability of solutes through a smart hydrogel.

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## Mechanical response of ultrastable glasses

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Mechanical response of amorphous solids is a fundamental research topic in glass science. Whereas amorphous solids respond elastically to a small strain (or stress), the system eventually yields at a large strain, showing plastic response. Although amorphous solids such as glasses are ubiquitous and relevant for industrial applications, understanding of mechanical response is still poor.

Computer simulations play an important role in this field, since they are able to provide atomic resolution of mechanical response of glasses. However, there are huge gaps in the accessible timescales between ordinary computer simulations and experiments in terms of glass preparation (e.g. cooling rate) and timescale of deformation (e.g. strain rate). Timescale of current computer simulations are about 10 orders of magnitudes smaller, behind as compared to that of experiments, which makes possible studies of poorly annealed glasses with very large strain rate  $\dot{\gamma}$ . For the strain rate, one can overcome the timescale gap by using the athermal quasi-static shear ( $\dot{\gamma} \rightarrow 0$ ) method which neglects thermal fluctuations [1]. However, fast cooling rate of ordinary simulations still prevents us from studying glasses in experimental condition.

Recently, we have developed very efficient simulation setup using particle swap Monte-Carlo algorithm with size polydisperse particles [2]. By applying this setup for a realistic glass-forming system in three dimensions, we produce very well-annealed glasses whose cooling rate is even slower than experiments, that is *ultrastable glasses*. We perform athermal quasi-static shear deformation on these systems. Aim of this work is to establish the first simulation study of mechanical response of glasses in and beyond experimental timescales in both cooling and strain rates [3].

Our athermal quasi-static shear simulation of the ultrastable glasses show qualitatively different behaviors from ordinary computer glasses [3]. 1) *Sharp yielding transition*: The stress-strain curve of the ultrastable glasses show very big stress overshoot and sharp yielding, which corresponds to shear band spanning entire sample. With the help of the finite size scaling, we unambiguously determine the yielding transition point at the thermodynamic limit. 2) *Burst of stress drops before yielding*: We observe sudden emergence of burst of stress drops slightly before the yielding transition point, which can be regarded as a precursor of the yielding. 3) *Strong persistent initial memory*: After the yielding transition, the systems do not converge to a steady state until more than 1000% shear strain, which is in stark contrast to ordinary glasses.

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## Structural characterization of relaxation of supercooled tetrahedral liquids in terms of boat and chair rings

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It is well established [1] that the relaxation of supercooled liquids modeled by Stillinger-Weber Potential [2, 3] across the limits of stability leads to a rapid increase in local tetrahedral order. To characterize the relaxation in detail, we propose a method to trace the particles with crystal-like local tetrahedral order. The method is based on the idea that crystal-like local fluctuations can be observed within specific medium range order (MRO) environments. In particular, we identify the particles in MRO structures defined by clusters of three 6-membered rings with the boat and the chair shapes. These rings shapes are specifically chosen because the stable hexagonal crystal phase is composed boat and chair rings in the 3:1 ratio. We introduce a criteria (based on internal dihedral angles) to identify the 6-membered rings with boat and chair shapes. We validate the average shape of the rings by computing the distributions of the Cremer-Pople ring puckering parameters [3, 4]. Among the various MRO clusters, we find that the particles which are common to two chair and one boat ring (ccb particles) have the highest local tetrahedral environment, followed by the particles common to three chair rings (ccc particles), and two boat and one chair ring (bbc particles). During the relaxation of the supercooled liquid across the instability, the relative changes in the number of these particles (ccb exhibiting the largest increase, followed by ccc and bbc) correlates well with the extent of local order. Further, we see a large increase in the cubic diamond (10-atom cluster with 4 chair rings) and hexagonal wurtzite (12-atom cluster with 3 boat and 2 chair rings) units with considerable interlinking. The diamond and the wurtzite units interconnect through a shared chair ring which is composed of 6 ccb particles. Since ccb particles are found to have the most crystal-like local tetrahedral order, we conclude that the stacking of cubic and hexagonal units is due to the tendency of the system to acquire local tetrahedral environment. Overall, we find that the relaxation across the instability is characterized by interlinking of mesoscale structures (boats, chairs, diamonds and wurtzites) which, in turn, signals an increase in the spatial extent of the structural correlations.

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# Calculation of displacement correlation tensor indicating vortical collective motion in two-dimensional systems of Brownian particles

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Studies on dense liquids, in the last two decades, have made it clear that the slowdown of diffusion in such systems is associated with emergence of collective or cooperative motions of numerous particles [1, 2]. This means that the cage effect should be understood not simply as a short-scale mechanism but as a part of collective dynamics on larger scales. Proper characterization and quantification of collective motions, in real liquids or model liquids such as systems of repulsive Brownian particles, are therefore crucial to theoretical clarification of the slow dynamics of dense liquids.

A popular approach to such collective motions is based on the microscopic density field,  $\rho(\mathbf{r}, t) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j(t))$ , where  $\mathbf{r}_j(t)$  is the position vector of the  $j$ -th particle at the time  $t$ . Four-point space-time correlations, such as  $\langle \rho(\mathbf{r}_1, t) \rho(\mathbf{r}_1, s) \rho(\mathbf{r}_2, t) \rho(\mathbf{r}_2, s) \rangle$ , reveal the presence of collective motions [2]. This approach, however, has a fundamental limitation: collective motions in liquids are often found to consist of swirls or vortices [3, 4, 5], while the density-based approach lacks a direct access to directional aspects of motions, as the density  $\rho$  is scalar. The vortical motions have been observed through another approach by means of the displacement of the particles,  $\mathbf{R}_j = \mathbf{R}_j(t, s) = \mathbf{r}_j(t) - \mathbf{r}_j(s)$ .

Here we report our analytical calculation of the displacement correlation tensor,  $\langle \mathbf{R} \otimes \mathbf{R} \rangle$ , for a system of two-dimensional repulsive Brownian particles [6, 7]. As a result, we have reproduced the vortex pair structure observed by Doliwa and Heuer [3]. Although the observed vortical structure may look similar to the one reported by Alder and Wainwright [8], there is an essential difference that the velocity autocorrelation has a negative longtime tail in the present case, as opposed to the positive Alder–Wainwright tail.

The key idea for the analytical calculation is based on what is called the Lagrangian correlation in fluid mechanics, consisting in adoption of continuous label variables. Both the longitudinal and transverse components of the displacement correlation are found to be expressible in terms of a similarity variable, suggesting that the cages are nested to form a self-similar, matryoshka-like structure in the space–time.

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## Cooling rate dependence of simulated Cu-Zr-(Al) metallic glasses structure

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Using molecular dynamics simulations, we study structure of Cu-Zr-(Al) alloys focusing on the compositions  $\text{Cu}_{64.5}\text{Zr}_{35.5}$  and  $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$  for which bulk metallic glass formation is observed. To describe interaction between particles the embedded atom model potentials developed in [1, 2] were used.

We systematically study the structural evolution of the systems during the cooling in a wide range of cooling rates  $\gamma \in (10^9, 10^{13})$  K/s. Investigating short- and medium-range order, we show that structure of Cu-Zr-(Al) metallic glasses essentially depends on cooling rate. In particular, a decrease of the cooling rate leads to an increase of abundances of both the icosahedral-like clusters and Frank-Kasper Z16 polyhedra.

For the  $\text{Cu}_{64.5}\text{Zr}_{35.5}$  system, the amounts of these clusters in the glassy state drastically increase at the  $\gamma_{\min} = 1.5 \cdot 10^9$  K/s. Analysing the structure of the glass at  $\gamma_{\min}$ , we observe the formation of nano-sized crystalline grain of  $\text{Cu}_2\text{Zr}$  intermetallic compound with the structure of  $\text{Cu}_2\text{Mg}$  Laves phase. The structure of this compound is isomorphous with that for  $\text{Cu}_5\text{Zr}$  intermetallic compound. Both crystal lattices consist of two type of clusters: Cu-centered 13-atom icosahedral-like cluster and Zr-centered 17-atom Frank-Kasper polyhedron Z16. That suggests the same structural motifs for the metallic glass and intermetallic compounds of Cu-Zr system and explains the drastic increase of the abundances of these clusters observed at  $\gamma_{\min}$  [3]. We show that the formation of  $\text{Cu}_2\text{Zr}$  compound is also observed during the isothermal annealing of the system at temperatures near the glass transition temperature. That means the  $\text{Cu}_{64.5}\text{Zr}_{35.5}$  alloy modeled by EAM potential developed in Ref. [1] may not be so good glassformer.

For the  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  system, the annealing at the temperature  $T = 850$  K (near glass transition temperature  $T_g$ ) also causes partial crystallization with the formation of the same  $\text{Cu}_2\text{Zr}$  compound as observed for  $\text{Cu}_{64.5}\text{Zr}_{35.5}$  alloy. This result is very interesting because the structure of  $\text{Cu}_2\text{Zr}$  has not been directly observed yet.

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## Crystallization kinetics of $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$ bulk metallic glasses

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The Cu-Zr system is in the short list of binary alloys capable to form bulk metallic glasses (BMGs) [1, 2]. The addition of a third element such as Al or Ti improves essentially glass forming ability of the Cu-Zr alloys as well as thermal stability of produced BMGs. The compositions of BMG formation in Cu-Zr alloys are located in narrow (so-called pinpoint) concentration intervals [2]. One such BMG-forming composition is the  $\text{Cu}_{50}\text{Zr}_{50}$  alloy which also demonstrates shape memory effects due to reversible martensitic transformation of B2  $\text{CuZr}$  intermetallic compound. The combination of high glass-forming ability and possibility of reversible martensitic transformation are the keystones of the formation of high-strength ductile composites with improved mechanical properties [3]. So the alloys with the compositions  $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{M}_x$ , where M is one or more metals, are the most promising candidates to form such composites.

We systematically study phase formation, crystallization kinetics, structure and thermal properties of  $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$  amorphous alloys in a wide temperature range by X-ray diffraction, calorimetry, dilatometry and optical microscopy methods. For  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  alloy, we find that, depending on cooling rate, it is possible to obtain BMG composites with different sizes of crystalline inclusions. Comparative study of the crystallization kinetics of  $\text{Cu}_{50}\text{Zr}_{50}$  and  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  amorphous alloys has been carried out for the first time using multivariate non-linear regression. We show that mechanisms of the crystallization of metallic glasses studied are substantially different and described by different models. The binary alloy crystallises by branched four-step reaction. For the ternary system, we propose two-step kinetic model of the crystallization process with consecutive reactions.

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Chemical potential is a key thermodynamic quantity in the study of liquid systems, regulating a wide range of phenomena, such as phase transitions and chemical reactions. The calculation of chemical potential in dense fluids represents a long-standing challenge in molecular simulations. In the classical techniques, building on Widom's method, chemical potential is computed by sampling the energy of insertion of a test particle. The largest contributions to the resulting estimate come from the low energy insertions, that is when the test particle is placed in a proper cavity within the system particles. In dense liquids such cavities are rarely available, and the sampling is mostly restricted to large insertion energies, strongly limiting the accuracy of the result.

Here I present a new method for computing the chemical potential in dense liquids [1]. This technique relies on a biasing approach that extends the insertion sampling to the relevant low energy region, inaccessible in unbiased simulations. The method is tested with both homogeneous and non-homogeneous Lennard-Jones fluids. As a result an accurate chemical potential estimate is obtained even at very large densities, when the classical approach lacks in efficiency and accuracy.

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## Heat transport coefficients from optimally short molecular dynamics simulations

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A new method is introduced to estimate transport coefficients in extended systems from optimally short equilibrium molecular dynamics simulations, based on the Green-Kubo theory of linear response and the cepstral analysis of time series. Information from the *full* sample power spectrum of the relevant current for a *single* trajectory is leveraged to evaluate and optimally reduce the noise affecting its zero-frequency value, whose expectation is proportional to the corresponding conductivity. Our method is unbiased and consistent, in that both the resulting bias and statistical error can be made arbitrarily small in the long-time limit. A simple protocol to evaluate thermal conductivities is finally proposed and validated in the paradigmatic cases of elemental and molecular fluids (liquid Ar and H<sub>2</sub>O) and of crystalline and glassy solids (MgO and  $\alpha$ -SiO<sub>2</sub>).

## **Topic 8**

# **Driven Systems, Rheology, Nanofluidics**

# Polymer flow and polymer topology: linear chains, rings and knots flow differently

9.001

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Modifications of the topological state of polymers are extremely interesting and relevant operations for a vast domain of scientific inquiry ranging from knot theory and polymer science all the way to materials science and biophysics, where cyclic and knotted DNA plays a key role in biological processes. Recent work has demonstrated that joining the two ends of a linear chain to form a cyclic (ring) polymer has a number of significant consequences in the structural [1, 2] and rheological [3] properties of concentrated or semidilute solutions of the same. Accordingly, a number of questions arise regarding the behavior of linear, cyclic and knotted ring polymers under flow: how does the topology of the dissolved polymer, in particular the knot complexity, affect its shape parameters and orientational resistance, as well as its rotation-, tumbling- or tank-treading motion under Couette flow? What consequences does shear flow have for knot localization along a sheared polymer? Can one make use of the different flow properties and distinct migration behaviour of various polymer topologies to build microfluidic devices that act as filters/separators of topologically different polymers? By applying hybrid (MPCD/MD) simulation techniques that take into account the hydrodynamics, we address the questions above for polymers of varying topologies, knottedness and stiffness. We analyze quantitatively the influence of polymer topology on the properties of single, fully flexible polymers under planar Couette flow [4]. These results are complemented by polymers' migration behaviour in a Poiseuille flow of varying shear gradient. On this basis we suggest the construction of topology-separating microfluidic devices [5].

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## Designing a topological filter: Transport of linear and ring polymers in micro-fluidic devices

9.002

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Ring polymers are an important class of biological and synthetic macromolecules. Due to the lack of free ends, they are expected to show distinct behaviour compared to their linear counterparts, as for example with respect to migration, rheology or disentanglement [1]. This simulation study aims at addressing the question whether those two are transported distinctly in micro-fluidic devices. Since many biological ring polymers are in aqueous solution, hydrodynamics is taken into account by a simulation method called Multi-Particle Collision Dynamics [2]. Although a bare slit channel is not sufficient to separate them for all investigated rigidities, we propose a filter by decorating the channel walls with attractive spots. In doing so, ring polymers show up to an order of magnitude increase in transport compared to linear chains. Moreover, those spots induce a reorientation of ring polymers close to the walls enabling them to perform a tank-treading motion along the patches [3]. At the same time, and for intermediate driving pressure gradients along the channel, a crossover regime appears in which the linear chains are transported faster than the rings due to incessant adsorption-desorption processes that are active for the former but not for the latter. Our work demonstrates the possibility to employ micro-fluidic devices in order to achieve separation of topologically distinct states of polymeric macromolecules.

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## Rheological properties of isolated telechelic star polymers under linear shear flow

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Telechelic star polymers (TSPs) are macromolecules formed by a number of diblock copolymers (arms) anchored to a common central core, being the internal monomers solvophilic and the end monomers solvophobic. Very recent studies [1-3] have demonstrated that TSPs constitute self-assembling building blocks with specific softness, functionalisation, shape and flexibility: depending on different physical and chemical parameters, e.g. number of arms  $f$ , solvophobic-to-solvophilic ratio  $\alpha$  and temperature  $T$  (solvent quality  $\lambda$ ). The geometrical conformation of TSPs features a well defined number of attractive spot on their surface. In this way, they can be considered as very tunable soft-patchy colloids and therefore can lead to the formation of well-controlled ordered and disordered phases in soft condensed matter systems. In this research, we systematically study the behaviour of isolated TSP under linear shear flow by means of a combination of Multi-Particle Collision Dynamics (MPCD) for the solvent and standard Molecular Dynamics (MD) for the monomers. We systematically evaluate the average star shape descriptors (gyration tensor), patches distinctive features and the rotation frequency as a function of the Weissenberg number ( $Wi$ ) for a wide range of parameters given by,  $f=18$ ,  $\alpha=0.3, 0.5, 0.7$ ,  $\lambda=1.0, 1.1$  and  $Wi<1400$ . We demonstrate that for low values of the  $Wi$  ( $Wi<10$ ) the geometrical properties and the patches behaviour of the TSP do not change, while  $Wi>10$  the radius of the gyration ( $R_g$ ), the asphericity ( $S$ ) and the relative shape anisotropy ( $\delta$ ) increases for most cases, from spheric-like ( $S\sim 0$  and  $d\sim 0$ ) to ovoid-like geometry (for  $Wi\sim 1400$  we find  $S\sim 1.5$  and  $d\sim 0.8$ ). Regarding patches behaviour, we find three different tendencies, depending on  $\alpha$  and  $\lambda$ , the number of patches can increase, decrease or remain the same as  $Wi$  increases. Since the conformation of a single TSP is expected to be preserved in low-density bulk phases, the presented results are a first step in understanding and predicting the rheological properties of semi-dilute suspensions of this kind of polymers.

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# Colloidal particles driven across an oscillating periodic optical potential energy landscape

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Driven Brownian particles travel across periodic potential energy landscapes, such as sinusoidal and ratchet potentials, in a manner that changes with the properties of the landscape [1]. These systems are sensitive to the driving velocity, as well as the wavelength of the landscape and the potential depth. With a sinusoidal potential, modulation of the driving force leads to synchronisation in the form of mode locking [2] and a similar phenomenon has been predicted for oscillating periodic potentials combined with a constant driving force [3]. Such periodic landscapes can be realised using optical tweezing, which allows precise manipulation of particles on the colloidal scale.

Here, we study the motion of a colloidal sphere as it is driven, at finely controlled velocities, across a sinusoidal potential energy landscape with a depth that is temporally oscillating. The one-dimensional potential energy landscape is generated by combining multiple optical tweezers and we use bright-field microscopy to track the particle movement. This allows us to study the dynamics of the system and observe synchronisation between the particle motion and the oscillations of the potential. In particular, we study how particle transport is affected as the nature of the landscape changes, in terms of the stepwidth, critical driving force and effective diffusion constants and we compare our results to Langevin simulations.

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## Viscosity of the Lennard-Jones fluid

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The steady-state shear viscosity of the Lennard-Jones (LJ) fluid has been evaluated at more than one hundred state points using the SLLOD algorithm, covering number densities  $\rho$  varying between 0.9 and 3.4 and temperatures  $T$  from the triple point temperature to several hundred (LJ units). Most of the state points studied are supercritical. The data are well described by the following equation for the (macroscopically) reduced viscosity,  $\tilde{\eta} = \tilde{\eta}_0 \exp[B (T_F(\rho)/T)^{2/3}]$  in which  $T_F(\rho)$  is the freezing temperature as a function of density and  $B = 2.37$ . This equation may be justified in part by reference to the isomorph theory [1,2], but the exponent 2/3 remains to be derived theoretically. The paper also reports data for the diffusivity, which violate the Stokes-Einstein relation at high temperatures. The findings are discussed in light of other representations of the LJ viscosity's variation throughout the phase diagram.

This work has not been published yet but is part of the PhD thesis in [3].

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## Experimental and simulated study of nearly-hard sphere suspensions in an oscillatory shear

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Both hydrodynamic and particle-particle interactions that depend on the flow-induced arrangement of particles to fragile structures, have contributions to the viscosity of a dense suspension below jamming. Here, we report an experimental and simulated study on nearly-hard sphere suspensions responding to an oscillatory shear in the athermal, non-inertial limit.

Three distinct regimes governed by the strain amplitude  $\gamma_0$  have been observed in this system. In the  $\gamma_0 < 10^{-1}$  regime, the particles remain separated and the suspension shows a Newtonian behaviour, with the shear stress proportional to the strain rate, and the normal stresses near zero. As  $\gamma_0$  goes up, the particle-particle contacts start to build up, and keep breaking and reforming throughout the entire oscillatory cycles, which indicates a non-linear regime that reveals the fragility of the material. When  $\gamma_0 > 10^1$ , the well-established microstructure appears at the beginning of each shear cycles and a quasi-Newtonian rheological behaviour is shown as the shear stresses varies with the rate, but flow-induced structures lead to non-zero normal stresses.

We further show that oscillatory shear may be used to isolate specific stress contributions in dense suspensions, and more generally in those materials whose rheology has contributions with both hydrodynamic and non-hydrodynamic origin.

# Nonequilibrium dynamic clustering of hydrodynamically coupled particles driven by optical force

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Recently, the collective motion of self-propelled micro-objects have been intensively studied experimentally and theoretically as active matter from the viewpoint of non-equilibrium physics [1]. In a micron-scaled system, since its Reynolds number is considerably small, the micro-objects often show characteristic collective motions via strong long-ranged hydrodynamic interaction between them. To elucidate those complex motions, it is necessary to study a simple model system to clarify the role of hydrodynamic interaction on their collective motion. In this study, we studied a one-dimensional system composed of optically driven small numbered particles and discussed the physical mechanism of their collective motion.

The multiple number of silica particles have been simultaneously driven by an optical vortex realized by a holographic optical tweezers [2]. We studied the change of their collective motion with varying their relative size in binary-sized system and the thickness of a container cell. In case of the thickness is much larger than the size of the particles, they form dynamic cluster or stationary cluster due to the hydrodynamic attraction promoted by the curved path [3, 4]. The formed clusters can be regarded as non-equilibrium one-dimensional crystal or cluster those cannot be formed in equilibrium state. With increase of the size ratio, the dynamic clustering and decomposition of clusters is replaced place by stationary clusters [4].

In a thin cell whose thickness is the same order of the particle size, a longer cluster with small velocity is relatively stable similar to traffic jamming on a highway. The front particle of the cluster only can leave the cluster and attach to the end of the cluster. This is partially due to that the flow induced by moving particles is difficulty to pass through a narrow gap between particles and walls. The transition between those two states due to the spatial confinement is discussed experimentally and theoretically.

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## DDM is a new track to microrheology, without tracking

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About 20 years ago, Mason and Weitz demonstrated in a pioneering work that the frequency-dependent mechanical response of a complex fluid can be effectively probed by monitoring the thermally excited positional fluctuations of tracer particles embedded in it, which marked the birth of microrheology [1]. Since then, microrheology has been the subject of intense investigation and development and, with different implementations, has progressively become a tool of choice for the characterization of local and bulk mechanical properties of viscoelastic fluids. The small required sample volume, the possibility of measuring extremely low elastic moduli and the access to multiple length scales are among the major strengths of microrheological methods. Thanks to all this, microrheology is nowadays routinely used in a wide spectrum of applications, ranging from colloid and polymer science to cell biophysics.

Microrheology relies on the accurate measurement, usually by optical means, of the displacement of probe particles or of some strictly related quantity. This information can be obtained for instance by reconstructing particles' trajectories directly in the real space, as done in Single Particle Tracking (SPT), or by measuring the fluctuations in the light singly (Dynamic Light Scattering, DLS) or multiply (Diffusing Wave Spectroscopy, DWS) scattered by the particles.

Here, we present a novel approach to microrheology that exploits Differential Dynamic Microscopy (DDM) [2], a microscopy-based method providing a quantification of the sample dynamics in the Fourier space [3]. As SPT, DDM operates on a sequence of microscopy images but, similarly to DLS, it provides an ensemble-averaged, wavevector-resolved information.

We performed experiments on both simple and viscoelastic fluids, seeded with tracer particles, exploring a wide range of sizes and concentrations. We show that, in all cases where also SPT can be used, DDM-based microrheology provide substantially equivalent results, with the benefit of a completely automated, operator-independent and unbiased image processing procedure.

Moreover, DDM microrheology is proven to provide a reliable information even in cases where SPT is not a suitable option, because the tracers are too small or too crowded to be tracked accurately. The simplicity and the robustness of our approach, as well as the possibility to easily extend the investigation to the rotational degrees of freedom of the probe particles [4] makes this method a viable alternative to SPT and to standard light scattering techniques for microrheology applications.

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# Dynamics of a Driven Colloidal Particle under Time-delayed Feedback Control

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Time-delayed feedback processes play an important role in the control and regulation of many stochastic systems, where interactions occur with a time lag [1]. Feedback processes of this type are often characterised by the flow of information. Here we use a driven colloidal particle under time-delayed feedback control to study the thermodynamic interplay between information and dissipation.

We present an experiment in which we optically manipulate a colloidal dumbbell of which one lobe experiences an attractive force and the other lobe experiences a repulsive force when placed in optical traps. The high refractive index lobe is trapped by a static optical trap, which then defines the centre of rotation for the low refractive lobe that is driven by a second dynamic optical trap. Importantly, the dynamic optical trap traces out the trajectory of the driven lobe with a given time lag.

Effectively, the driven lobe represents a 1D Brownian particle confined to a ring, driven out of equilibrium as it interacts with its ‘past self’ via the chasing dynamic trap. Numerical modeling of the experiment suggests that the dissipation is a non-monotonic function of the time lag, and achieves a maximum at a finite lag time, before asymptotically approaching a constant limit. Our theoretical analysis shows that the mutual information between the positions of the driven lobe and the dynamic trap has a minimum at a finite lag corresponding to the maximum dissipation. We will discuss the rich dynamics observed in our experiments as the time lag is varied and compare them to our theoretical and numerical findings.

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## Brillouin viscoelastometry of hydrocarbon binary mixture liquids

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To predict behavior of multicomponent fluids it is very important to understand their viscoelastic properties. From the practical point of view to monitor in real time viscosity and compressibility of multicomponent reservoir fluids is essential for effective extraction of downhole crude oil. The objective of this work is to explore applicability of laser-based Brillouin light scattering (BLS) spectroscopy to measure remotely bulk viscosity and excess compressibility of hydrocarbon binary liquids. BLS spectra were detected using high-resolution scanning six-pass tandem Fabry-Perot interferometry coupled with single photon counter. BLS measurements enable non-contact and remote assessment of viscoelastic properties of crude oil-benzene and other crude oil-aromatic hydrocarbons mixtures.

From measured densities, refractive indices, Brillouin spectral peak linewidths and positions we have evaluated the bulk viscosity and excess compressibility of binary liquid mixtures as a function of their corresponding component's volume fraction. Position and shape of Brillouin peaks change in binary mixtures across corresponding volume fractions. It is well known that the bulk viscosity can be determined from measured sound speed and attenuation. A broad linewidth of spontaneous Brillouin scattering peak is observed when a bulk viscosity is high in binary mixtures while sharp peak is observed when a bulk viscosity is low. Measured full spectral peak's full widths at half maximum (FWHMs) for crude oil-benzene mixtures monotonically decrease with the increase of benzene concentration. This variation is due to corresponding decrease in viscosity of the medium. The excess compressibility  $\beta_{ex}$ , defined as the difference between measured and ideal values of adiabatic compressibility, is calculated across the whole composition range of binary liquid components. With the increase of benzene concentration, measured density and refractive index of crude oil-benzene mixtures decrease almost linearly while the Brillouin peak frequency shifts nonlinearly. Observed positive deviation in  $\beta_{ex}$  of crude oil-benzene reaching maximum at ~ 60 % of volume fraction is largely attributed to similar behavior in the Brillouin peak frequency shift, which implies that repulsive interactions between the unlike molecules in the mixtures take place. Observed variations in viscoelastic properties of investigated hydrocarbon binary mixtures will be discussed in terms of intermolecular interactions and measured physico-chemical parameters.

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## Resilience of a thermoresponsive rod-like gel.

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Gel like products are omnipresent in foodstuff, building and geological material. Their solid like properties enable them to bear their own mass and those of fillers, that may be added to increase the overall elastic properties of those viscoelastic systems.

Successive shearing events may decrease, or even suppress, particle-bearing properties [1]. This may be the case when shearing the gel irreversibly changes its structure. Such effects are not desirable for consumer products, in which fillers should stay homogeneous in solution during process and shelf life.

For this reason, model systems are sought for in order to understand better the recovery of gel macrorheological properties in the presence of inclusion(s).

Such yield stress fluids are often composed of anisotropic sub units, such as colloidal rods or stiff polymers. Gel-like model solutions of attractive rods were obtained by grafting a thermoresponsive polymer, poly (N-isopropylacrylamide) [2], [3] on fd virus, a biological rod like model [4]. With increasing temperatures the coated rods become increasingly hydrophobic, leading to the formation of a gel of increasing strength. The properties of this physical gel can be further tuned by modifying electrostatic interactions, concentration and solvent affinity. We'll evidence in this poster the variation of moduli values and yield strains of poly(N-isopropylacrylamide) coated fd virus solutions after successive yielding events as well as its recovery, as a function of ionic strength and concentration.

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## Friction controls submerged granular flows

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The coupling between the interstitial medium and granular particles provide surprising surging dynamics in hopper flows [1]. The constant flow rate in dry cases and the increasing flow rate in submerged conditions are modeled in numerical simulations using computational fluid dynamics and discrete element method.

The coupling between liquid and particles consists only on pressure, drag and shear stress. We find that the simulation matches the experiments with exceptional accuracy and the inter-particle, coulomb, friction is surprisingly similar despite the assumed lubrication effects.

The role of friction is not clear in granular systems. The origin and value of friction coefficient and even whether its constant or not is still open for debate [2,3]. Here we show that in numerical simulations submerging the hopper changes the particle-particle contact friction from the vacuum value of  $\mu_v = 0.15$  to submerged value of  $\mu_s = 0.13$  while all the other simulation parameters stay the same. This tiny change in material parameters is a remarkable result as the qualitative and quantitative behavior of the flowing granular media changes dramatically [4,5]. The tiny change in is also remarkable when compared how the friction coefficient changes when the granular media is approximated as continuum with inertial effects [6,7]. Comparing the results between experiments and different numerical models for friction reveals the effect and magnitude of roughness, lubrication, dynamics and interstitial medium in the flow of discrete particles.

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# Non-Newtonian behavior of hydrated polymer under shear with ultrasmall amplitude

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Non-Newtonian behavior of fluid is generally attributed to its molecular-scale structure and dynamics. Recent progress in measurement techniques provides approaches to the microscopic aspect of the phenomena with unprecedented directness. With cutting-edge technique of atomic force microscopy (AFM) it is possible to carry out oscillatory shear study with subnanometer-level amplitude. By changing the amplitude viscoelastic response of fluid can be resolved with its internal length scales.

Hydrated bio-compatible phospholipid polymer 2-methacryloyloxyethyl phosphorylcholine (MPC) was reported to exhibit shear thinning at a shear amplitude of the order of 10 nm[1]. Here further analysis was carried out with the shear amplitude reduced down to sub-nanometer range using a home-built AFM apparatus[2] with noise level suppressed to the theoretical thermal limit. Well-characterized shear oscillation with ultrasmall amplitude was induced to a borosilicate glass sphere attached to an AFM cantilever[2]. Viscoelasticity of the hydrated MPC layer between the sphere and a Si substrate was measured together with the loading force. The shear amplitude was swept by about 2 orders of magnitude at several loading conditions and profile of relaxation time calculated from viscoelasticity was derived. The obtained profiles exhibited a dramatically discontinuous and discrete nature of the polymer-liquid complex, unlike smooth and continuous ones usually obtained for macroscopic shear measurement. They are classified into three characteristic regimes depending on the shear amplitude. In the first regime with peak-to-peak amplitude greater than ca. 0.24 nm it shows unstable binary oscillation with the gap opening up with amplitude decrease. In the second regime with amplitude of 0.06-0.24 nm the instability ceases and the profile exhibits a binary splitting. In the third regime with lowest amplitude the binary nature completely ceases. It is also found that major parts of the first and second regimes consist of quasi-Newtonian plateaus separated by discontinuous jumps.

The present findings are similar to amplitude-dependent discontinuity in frictional properties reported for solid friction studies[3,4], where the critical amplitude corresponds characteristic length scale in the sample, i.e. atoms or molecules. Thus the present result is considered to reflect structural and dynamical hierarchy in the hydrated polymer.

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## Rheological properties of mixtures of anisotropic colloids using molecular dynamics and stochastic rotation dynamics

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Self-assembly of mineral aggregates is a process of key relevance in nature and industry. In self-assembly, building blocks consisting of colloidal particles with anisotropy in shape and interaction form specific structures during aggregation. Transport and mechanical properties are strongly correlated with the properties of the colloids and their aggregates. An example is the binding phase of cement, calcium silicate hydrate (C-S-H). Early models of C-S-H proposed a building block of a few nanometers, which forms larger units up to 100 nm during hydration [1]. Experimental evidence has resolved the structure of these colloidal particles as calcium silicate sheets bound together by water, which resemble narrow disks that stack together to form larger globules [2]. Another example of industrial interest is calcium carbonate suspensions, where it has been shown that the rheological properties are strongly correlated with the microscopic structure [3], and the presence of organic additives can largely influence flow behaviour [4].

Using computer simulations, we explore the rheological properties of a suspension of colloidal particles targeting the characteristics of mineral aggregates. Due to the large colloid-solvent size ratio, we focus on mesoscopic simulations of colloids with spherical or aspherical shape, and with interactions that can be anisotropic. The solvent is modelled using stochastic rotation dynamics (SRD) [5], a method that includes thermal fluctuations and hydrodynamic interactions. We compute the shear viscosity using a reverse nonequilibrium method that allows us to explore the dependence of the shear viscosity on the inter-particle interactions, the composition of the suspension, and the shear rate. We confirm that the nonequilibrium method can be used to compute the shear viscosity of hard spheres, modelled through a repulsive power law. We find the well-known Einstein relation between shear viscosity and volume fraction at low concentrations, and its asymptotic behaviour near the jamming transition. The shear viscosity shows a strong dependence on the velocity gradient, with both shear thinning and shear thickening regimes. For binary mixtures of spheres with different sizes, we find that the shear viscosity of the mixture decreases with respect to the pure systems, as a function of the volume fraction and relative sizes of colloids. This effect connected to the increase in the maximum packing fraction before the jamming transition [6].

Tailoring the effective potentials between mineral building blocks with organic molecules, as well as the composition of the suspension, can lead to a desired rheological response. This investigation provides insight into the impact of additives on surface functionalization. The effective potentials between the colloids can be constructed from full atomistic simulations, bridging together the molecular and mesoscopic scales.

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In soft matter systems, one often is confronted with macromolecular objects dissolved in a fluid. Usually, the particles that make up the latter are significantly smaller and lighter than the macromolecules. This in turn induces that the two components have different time- (e.g. typical relaxation times), length-, or mass-scales which might differ by several orders of magnitude.

As such, atomistic simulations of large ensembles are sometimes prohibitively expensive. Given the disparity in the aforementioned scales, one possibility to deal with this issue is to neglect the solvent; however, one needs to take particular care along that route not to distort, or entirely lose access to, those phenomena that are characteristic for soft matter systems, which often arise from the very interplay between the two types of components.

One such prominent phenomenon is that of viscoelasticity, or non-Newtonian flow, where the viscosity of the solute-solvent-mixture depends on the local shear stress. We present a generalization [1, 2, 3] of the mesoscopic Multiparticle Collision Dynamics (MPC) algorithm [4, 5], which enables simulations of large systems of macromolecules dissolved in an effective, but explicit, solvent. This allows the solvent to mediate hydrodynamic interactions in a computationally highly efficient way.

The extension presented amounts to linking effective solvent particles via harmonic potentials to form coarse-grained polymers; their elastic degrees of freedom give rise to shear-dependent phenomena. The resulting MPC fluid is, given a suitable degree of polymerization, tantamount to a simplified model of a polymer melt, and exhibits intrinsic viscoelastic behavior. This enables MPC studies of other dissolved particles, such as colloids, in inherently non-Newtonian solvents.

We discuss the relationship between system parameters (i.e., the length of the effective polymers and interaction strength), and characteristic properties of the system. In particular, we focus on the velocity autocorrelation function in Fourier-space,  $\hat{C}_V^T(\mathbf{k}, t) = \langle \tilde{\mathbf{v}}(\mathbf{k}, t) \cdot \tilde{\mathbf{v}}(\mathbf{k}, 0) \rangle$ . From the analysis of this function we are able to extract information on a wide spectrum of properties, such as viscosity, diffusion behavior, polymer relaxation times, and the rheology in the long-time limit. We present an analytic (Rouse-based) formalism that allows one to calculate within suitable approximations  $\hat{C}_V^T$ ; this framework offers the possibility to efficiently tune the input parameters to match desired characteristic features in the correlation function. An excellent qualitative and quantitative agreement of the theoretical predictions and the simulation data can be reported.

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# Electro-osmotic flow and Droplet Electrophoresis in a bicomponent fluid

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Electroosmosis and electrophoresis are two important phenomena that take place in microfluidic devices, and both arise from the coupling between the electrostatic and the hydrodynamic interactions between the charged particles in solution. Even though electroosmosis and electrophoresis are often seen as different effects, there is in fact no fundamental distinction between the two. Here we show that one can indeed find a continuous transition between the two limits of a purely electroosmotic and of a purely electrophoretic motion for a fluid droplet in a nanochannel. In particular, we investigate the dependence of the mobility of a droplet on the solvation free energy of ions using a bicomponent Shan Chen fluid coupled to molecular dynamics, showing that it is possible to extract the electroosmotic contribution to the electrophoretic mobility of the droplet.

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## From collective transport to temperature gradient driven coarsening in near critical binary mixtures

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Recently, critical demixing transitions in binary liquid mixtures have gained significant renewed attention in the context of critical Casimir forces and of non-equilibrium active Brownian motion of colloidal particles, caused by temperature gradient driven local demixing in binary liquid solvents. Concerning static and dynamic critical behavior in *bulk*, we have employed a combination of Monte Carlo simulations in the semi-grand canonical ensemble and large-scale molecular dynamics simulations for a family of five symmetric binary Lennard-Jones mixtures (belonging to the so-called model H' dynamic universality class). Implementation of graphic processing units accelerators has made it possible to explore huge system sizes such that finite-size scaling has become less important for determining the relevant critical singularities. The static quantities studied here encompass the bulk phase diagram, the correlation length, and the concentration susceptibility, of the finite-sized systems above the bulk critical temperature  $T_c$ , the compressibility and the pressure at  $T_c$ . Concerning the collective transport properties, we focus on the Onsager coefficient and the shear viscosity. The critical power-law singularities of these quantities are analyzed in the mixed phase and non-universal critical amplitudes are extracted. Two universal amplitude ratios are calculated. Our results are compared with available theoretical and experimental predictions [1]. Concerning critical dynamics in the presence of a *surface*, we have employed mesoscopic numerical simulations and analytical theory in order to investigate temperature-gradient induced coarsening around a colloidal particle immersed in a binary solvent. Our phenomenological model turns out to capture recent experimental findings according to which, upon laser illumination of a Janus colloid, the surrounding binary liquid mixture develops a concentration gradient. Striking differences in the coarsening mechanism are observed depending on the composition of the fluid and on the adsorption preferences of the colloid. For an adsorptionwise neutral colloid, an interesting, critical relaxation induced crossover occurs concerning the phase formed on its surface. This crossover is absent for colloids with strong adsorption preferences. A Janus colloid, with a small temperature difference between its two hemispheres, reveals asymmetric structure formation and surface enrichment around it even if the solvent is within its one-phase region and the temperature of the colloid is above the critical demixing temperature  $T_c$ . A comparison between the surface patterns above and below  $T_c$  is provided [2].

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Power functional theory is a variational approach for the dynamics of many-body systems. The theory operates on the one-body level of correlation functions, such as the local density and the current distribution, and is based on an exact minimization principle. The original derivation addressed overdamped Brownian systems [1] as a simple model for colloidal dynamics. Recent extensions include the treatment of nonrelativistic quantum systems [2] and of inertial Newtonian dynamics [3]; the latter being relevant for Molecular Dynamics of atomic liquids. The central object of the theory is an excess (over ideal gas) intrinsic power functional that arises from internal interactions between the particles. For Brownian Dynamics, we show that explicit approximations can be systematically constructed [4] and test these against computer simulation results. The theory describes correctly the superadiabatic forces, which were shown to contribute significantly to the dynamics [5], and which are neglected in dynamical density functional theory [6].

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## Granular Mpemba effect: A hotter granular fluid can cool faster than a cooler one

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The Mpemba effect is a counterintuitive phenomenon according to which, given two samples of fluid, the initially hotter one may cool more rapidly than the initially cooler one [1, 2]. A necessary condition for the effect to take place is that the thermal rate of change depends not only on the instantaneous temperature but also on additional variables.

In this work, we show that the Mpemba effect is present in granular fluids, both in the uniformly heated and in the freely cooling systems [3]. By assuming that the most relevant variable to determine the thermal rate of change, apart from temperature itself, is the excess kurtosis of the velocity distribution of the grains, we obtain analytical quantitative predictions for how differently the system must be initially prepared to observe the effect. An inverse Mpemba effect [4] (whereby a cooler fluid heats more rapidly than a hotter one) is also predicted in the case of uniformly heated systems. The theoretical predictions are numerically confirmed by the direct simulation Monte Carlo method and by molecular dynamics.

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## Threshold force to melt a glass locally: Theory and Simulations of microrheology on a colloidal glass

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When a glass is subjected to an external shear stress, it melts if the stress is larger than the yield stress. In microrheology, an analogous phenomenology can be observed when an external force is exerted on a single particle, or probe [1]. Namely, if the force is too low, the probe is trapped and cannot escape its cage of neighbours, whereas large probe displacements (at long times) are observed for large forces. From a microscopic point of view, the most interesting case is where probe and bath particles are comparable in size, what can be achieved experimentally using a colloidal glass, with magnetically or optically driven probes.

In this work, we present theory and simulations concerning the probe localized – delocalized crossover in a colloidal glass of hard spheres. In the theory, we model the dynamics of the glassy bath and probe with mode coupling theory (MCT), based on the Smoluchowski equation. Multiple relaxation channels are considered in a matrix formulation, to account for the anisotropy in the probe dynamics. In the simulations, all particles undergo Langevin dynamics, including the probe. The two regimes are obtained in the theory, and a critical force can be identified as a sharp crossover between them. The probe position distribution functions and correlation functions predicted by the theory are confirmed by simulations in the localized probe regime [2]. Simulations also provide useful insights into the dynamical heterogeneities of the bath, or the effects of the pulled probe. We also study the properties around the critical force, namely, a power-law decay of the probe position correlation function, corrections to this power law and heterogeneous dynamics. The results confirm the validity of the theory model, and give further evidence of the utility of microrheology to rationalize the microscopic properties of fluids and glasses.

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In this work, we study the non-equilibrium electrolyte kinetics in a planar nanocapacitor, which is driven by periodically switching surface charges using scaling theory and simulation. We show that the combined effects of inter-ionic charge correlations and hydrodynamic interactions lead to correlated convective behavior for weakly charged ions. These dynamic correlations, signalling the breakdown of Poisson-Nernst-Planck (PNP) theory, are distinct from static correlations that are manifested by the crossover from Poisson-Boltzmann to strong coupling theory that occurs as the ion valency increases [1].

We derive a simple scaling relation for the crossover from individual ion diffusion to collective (convective) motion in external field  $E$ . For this we compare the electrophoretic speed  $V_R$  of a convective roll of radius  $R$  with the speed of a single ion  $V_0$ . Electrolyte charge  $Q_R$  in a volume of radius  $R$ ,  $Q_R \sim eqc_s R^3$  ( $e$  is the elementary charge,  $q$  ion valency,  $c_s$  ion concentration) moves in the external field with Stokes' friction  $\eta V_R$ , so that  $V_R \sim Q_R E / (\eta R)$ . If the ion concentration is set by the electrode charge density  $\sigma_0$  and distance between the electrodes  $d$ , we find  $V_R \sim e\sigma_0 R^2 E / (\eta d)$ . The corresponding estimate for a single ion yields  $V_0 \sim eqE / (\eta a)$ , where  $a$  is the ion radius. Convection is expected to emerge when the speed  $V_R$  and thus the electric current associated with the motion of a convective roll of size  $R$  is greater than  $V_0$ , i.e. in the case  $V_R > V_0$  or  $\sigma_0 R^2 / d > q/a$ . We introduce two dimensionless parameters: the ion coupling parameter  $\zeta = q^2 \lambda_B / a$  ( $\lambda_B$  being the Bjerrum length) and the rescaled surface potential  $\Psi = 2\pi\sigma_0 q d \lambda_B$ . Using that the typical size of a convective roll is given by the capacitor distance  $d$ ,  $R \sim d$ , we obtain the condition for onset of convection as  $\zeta < \Psi$ . This scaling law describes the dynamic breakdown of PNP theory, according to which charge transport in a planar capacitor system is described by an ion velocity distribution that is uniform in the lateral direction. The convection constitutes a pronounced deviation from a laterally homogeneous velocity distribution. Similar mechanisms govern electroconvection in charged colloidal systems [2], and also Rayleigh-Benard convection, where it competes with diffusive heat transport [3]. A similar instability is observed in colloids, where lateral particle segregation of driven colloids leading to laning is reported [4].

We use hybrid Molecular Dynamics - Lattice Boltzmann simulations to demonstrate the formation of convective rolls as predicted by the theory. The collective behaviour is characterised by velocity and position structure factors measured as a function of time. The crossover is predicted to happen at frequencies of at least  $10^5$  Hz in aqueous electrolytes.

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Flow of dilute polymer solutions is known to exhibit purely elastic instabilities even in the case of negligible fluid inertia. Such instabilities are observed and studied in flow with curvilinear streamlines, and are attributed to the generation of elastic stresses due to the stretching of polymers in the flow. We observe two elastic wake instabilities, in a creeping viscoelastic channel flow between two widely-spaced cylinders, which are associated with breaking of time-reversal and mirror symmetries: Hopf bifurcation and forward stationary, respectively. We suggest that a decrease of the normalized distance between the obstacles leads to a collapse of the two bifurcations into co-dimension two point, a situation general for many non-equilibrium systems. Further, we find a novel mechanism of the vorticity growth via increase of a vortex length in a viscoelastic flow in contrast to a well-known suppression of the vorticity in a Newtonian flow by polymer additives.

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Understanding complex fluids far from equilibrium is of fundamental and technological interest. The linear response of systems mildly perturbed from equilibrium can be understood in terms of the well known fluctuation-dissipation-theorem (FDT): The response is related to the fluctuations of the unperturbed system. For stronger perturbations, i.e., far from equilibrium, the situation is generally less clear, and is the topic of manifold ongoing investigations.

We present our recent progress in understanding far-from equilibrium fluids from the view point of statistical physics: Based on a path-integral version of nonlinear response theory [1], we demonstrate experimentally that the nonlinear (second order) response of an experimental model system can be determined from its fluctuations in equilibrium [2], which can be seen as an extension of the FDT to nonlinear responses. We also discuss how these insights may be employed to derive an effective (Langevin-)description for nonequilibrium complex fluids [3].

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## Nonlinear motion in viscoelastic media

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The investigation of driven colloidal particles in non-equilibrium baths, realized by viscoelastic solvents, is a promising new research topic in the field of Brownian motion. Due to the large relaxation times of viscoelastic media the driving of a colloidal particle leads to a genuine non-equilibrium system where (macroscopically) many degrees of freedom are out of equilibrium. In this non-equilibrium state the nonlinear response of the bath is of great importance [1] and a variety of non-equilibrium effects is expected to occur [2].

In this presentation, we review the current state of the art in the field of Brownian particles in non-equilibrium solvents. We discuss the significance of these kind of systems and demonstrate how to treat them in a theoretical approach. The identification of universal features of the dynamics of driven particles in non-equilibrium baths provides further incentive to study such systems.

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## Monolayers of hard rods: A soft matter model for non-equilibrium growth

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We model purely hard rods at the vicinity of a substrate both in a lattice model, where position and orientation of rods are restricted, and in a continuum model with hard spherocylinders, where both position and orientation are continuous variables. In a systematic, two-part study combining analytic theory and simulation we have determined the properties of these monolayers in *equilibrium* [J. Chem. Phys. **145**, 074902 (2016)], as well as in *non-equilibrium* under conditions of monotonic growth by means of random deposition [Klopotek et al., J. Chem. Phys., *accepted* (2017)]. Special attention is given to the orientational ordering of the rods: our generic model showcases the “standing-up” transition found in molecular thin film growth, e.g. with organic molecules, which are rod-like in shape, both in experiment [1] and in recent simulations [2]. The transition from ‘lying’ to ‘standing’ is thermodynamically *continuous* with hard rods both on the lattice and in the continuum. It remains so for a strong, orientation-dependent attractive substrate; however, this introduces spatio-temporal correlations during non-equilibrium growth: the self-assembly becomes sensitive to the diffusion coefficient of the rods at the substrate. Details of monolayer growth are relevant for the cases of Frank–van–der–Merwe (layer-by-layer) and Stranski–Krastanov (islands-on-layers) growth: in ongoing simulations of multi-layer growth, we recover the standing-up transition in the monolayer regime before further layers self-assemble. Slow monolayer growth is characterized by dynamic observables approaching a *quasi-equilibrium* master curve. Both models—lattice and continuum—in fact reveal qualitatively the same ensemble behavior during highly non-equilibrium growth, differing only via their respective equation-of-states. We discuss how mapping dynamic quantities between models means matching microscopic and macroscopic time-scales non-trivially.

Our equilibrium studies employ Monte Carlo (MC) simulations in the Grand Canonical ensemble, classical lattice Density Functional Theory (DFT) for lattice systems [3], and continuum MC simulations; in non-equilibrium, kinetic Monte Carlo, dynamic DFT on the lattice, and dynamic MC for Brownian dynamics in the continuum were employed.

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## Rheology of Pluronic-Hyaluronic acid thermoreversible gelling systems

9.026

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Pluronic F-127 is a triblock copolymer that exhibits thermoreversible sol-gel transition contributed by the formation of micelles that self assemble and subsequently form a close packed cubic structure. Systems of pluronic with polysaccharides are generally considered to enhance gel stability and mechanical strength for controlled drug delivery applications. This study aims at elucidating the gelation behavior and structure-property relationship of pluronic (PI) in the presence of Hyaluronic acid (HA) using rheology. HA increased the width of gel transition in PI-HA systems as opposed to the sharp transition in case of PI. Small amplitude oscillatory shear indicated weak frequency dependence of  $G'$  and  $G''$ . Strain rate frequency superposition (SRFS) was performed to probe their low frequency structural relaxation. Large deformation response indicated shear induced yielding with both the moduli following power law decay beyond the critical strain amplitude.  $G''$  exhibited a well-defined peak just before the decay, a typical characteristic of soft glassy materials/soft solids. Stress waveform analysis, Fourier and Chebyshev decomposition to obtain higher harmonics and intracycle measures indicated similar qualitative features, though interestingly, there is a non-monotonic increase in the yield stress (at nearly same yield strain) and  $G'$  with HA content. An Elasto-visco-plastic model is shown to simulate nonlinear response of the systems.

## The analog of discontinuous shear thickening flows under confining pressure

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We use 2D numerical simulations to study dense suspensions of non-Brownian hard particles using the Critical Load Model (CLM) under constant confining pressures. At constant packing fraction this simple model shows shear thickening as the tangential forces get activated upon increased shear stresses. By parameterizing a simple binary system of frictional and non-frictional particles of different proportions we show that the jamming packing fraction, at which the viscosity diverges, is controlled by the fraction of frictional contacts. The viscosity of dense suspensions can thereby be expressed as a function of the fraction of frictional contacts as well as the packing fraction of solid particles. In addition, we show that there exists a simple relationship between the fraction of frictional contacts and the two control parameters (under confining pressure): the viscous number  $J$  and the ratio between the repulsive barrier force and confining pressure. Under confining pressures the viscosity curves are found to depend on the shear protocol, with the possibility of yielding negative *dynamic* compressibility, an analog to the discontinuous (DST) shear thickening found at high but constant packing fractions for the same system.

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Dense colloidal suspensions in strong spatial confinement under shear display complex non-equilibrium dynamics [1, 2, 3]. Understanding the dynamical- and rheological response of these soft materials at the nanoscale is key for various applications [3, 4].

Here, we perform overdamped Brownian dynamic (BD) simulations of strongly confined suspensions of colloids under shear in a circular two dimensional geometry. In particular, we consider a system consisting of two individually driven rings, confining additional particles between the inner- and the outer ring (Taylor-Couette geometry), resembling a clutch at the nanoscale. We find that the impact of hydrodynamic interactions on the dynamical as well as the rheological response are key and can not be neglected. In fact, the inner ring is driven by the translation-rotation coupling due to hydrodynamic interactions. We identify the dominating transport mechanisms governing the overall dynamics of the system and determine the rheological response.

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# **Topic 10**

## **Active Matter**



## Emergent forces in active hard spheres

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Most colloidal interactions can be tuned by changing properties of the medium. Here we show that activating the colloidal particles with random self-propulsion can induce giant emergent effective interactions between large objects immersed in such a suspension [1]. By performing Brownian dynamics simulations, we systematically study the effective force between two hard walls in a 2D suspension of self-propelled (active) colloidal hard spheres. We find that at relatively high densities, the active colloidal hard spheres can form a dynamic crystalline bridge, which induces a strong oscillating long range dynamic wetting repulsion between the walls. With decreasing the density of active colloids, the dynamic bridge gradually breaks, and an intriguing long range dynamic depletion attraction starts dominating the effective interaction between the two walls. The two long range forces oppose each other, and the effective interaction can be tuned from a long range repulsion into a long range attraction by reducing the density of active particles. Our results open up new possibilities to manipulate the motion and assembly of microscopic objects by using active matter.

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# Dynamical coupling between structural rearrangements and self-propelled particle motion in colloidal glasses

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It has been recently demonstrated that the glass transition of dense colloidal suspensions is progressively shifted by increasing activity of embedded self-propelled particles (SPP) [1]. However, it is not clear yet, how the dynamics of such SPP becomes affected by the surrounding glassy environment. We experimentally investigate the active motion of spherical Janus particles within a cage created by a binary mixture of colloidal particles. We observe a dramatic enhancement of the rotational diffusion of active particles with increasing particle velocity and the density, in a similar fashion as SPP in semi-dilute polymer solutions [2]. This experimental approach allows us to measure, in parallel, the temporal evolution of the active particle and the passive colloidal suspension. Our findings suggest that these effects originate from the coupling between the thermal fluctuations of the particle and the surrounding heterogeneities, which displays large relaxation times of several seconds.

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## Modular Micro-Swimmers

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Creating the next generations of microswimmers, capable of taking up multifunctional tasks, poses a significant challenge to the experimental community. We take a modular approach to self-assemble inactive components into moving complexes, rather than relying on single self-propelled entities. The central part of modular micro-swimming are ion-exchange resin (IEX) particles that induce electroosmotic (eo) flow along a charged surface [1]. A mobile IEX can assemble and couple colloidal (cargo) particles, which in turn break the flow symmetry, thus leading to propulsion of the whole self-assembled complex. Such minimal modular swimmers move at velocities of several  $\mu\text{m/s}$  over extended times [3,4]. Interestingly the complex velocity increases in steps with increasing number of cargo particle, but saturates, when the maximum number of first row cargo is reached. This is captured by a simple geometric model, where a maximum first-row opening angle of cargo particles determines the shape of velocity curve [3]. The flexible attainable combination of modular approach allows us to assemble colloidal crystals [2], “colloidal molecules” with long range attractive interactions [5], and “paddle steamer” type micro-swimmers with dynamic 3D structure.

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The efficient self-propulsion of bacteria has inspired the development of bacterial-based bio-hybrid microswimmers. These are realized by integrating bacteria with artificial elements, which has potential medical applications such as transport, sensing, and manipulation [1,2]. The microswimmers developed here are in the form of micron-sized silica Janus spheres (3  $\mu$ m diameter), coated from one side with gold caps (30 nm thickness) and bacteria attached to the gold side. The partial gold coating, and subsequent selective bacterial coverage, leads to a directional propulsion of the microswimmer. The bacteria are attached to the spheres through membrane–protein binding to a biotin–streptavidin coating of the Janus spheres, where the difference in the binding affinity of streptavidin to silica and gold allows for only the gold-coated area to be functionalized with streptavidin [3]. The behavior of the bio-hybrid microswimmers is studied in a simple harmonic optical potential, as well as in more complex optical potentials using speckle light fields [4,5]. The displacement of the microswimmers is compared to the diffusion length of the Janus spheres without bacterial adhesion to confirm that the displacement is due to bacteria propulsion, not to Brownian motion.

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# Phase co-existence in bidimensional passive and active dumbbell systems

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It has been recently argued[2] that  $2d$  melting of hard and soft repulsive disks occurs in two steps, with a continuous BKT transition between the solid and hexatic phases, and a first order transition between the hexatic and liquid phases, when density or packing fraction are decreased at constant temperature.

In recent years, interest in the behavior of these and other  $2d$  (and also  $3d$ ) macroscopic systems under continuous and homogeneous input of energy increased due to their connection with active matter[3]. Very rich collective motion arises under these out of equilibrium conditions, and liquid, solid-like and segregated phases are observed. I will present results showing that, notably, segregation exists *not only* for large values of the activity. The region of co-existence under activity continuously links to the phase predicted by Bernard & Krauth[2] in the passive limit (figure1 in [1]).

We support our claim with a detailed numerical analysis of the dynamics of a bidimensional purely repulsive dumbbell system[1]. The reason for this choice of model is that many natural swimmers have elongated shape and the simplest model of an anisotropic particle is a dumbbell. This geometry favors aggregation, even in the absence of attractive forces, at intermediate densities and sufficiently strong activation[3]. In this limit the evolution of an initial homogeneous phase occurs by nucleation and growth of clusters and the system phase separates. At the other extreme, for sufficiently low densities and not so strong activity, particles form only very small clusters that do not coalesce. The results obtained complement these two extreme limits. In the absence of activity we confirm the scenario of Bernard, Kapfer & Krauth, for hard and soft disks[2] using now a molecular system. We estimate the density interval for co-existence. Switching on activity we prove that this interval *continuously expands* towards the strong activity region where cluster aggregation had already been observed. There is therefore no discontinuity between the passive and active regions in the phase diagram with phase separation. Figure1 in [1] summarises this scenario that is different from what has been stated in the literature so far.

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## Towards Van 't Hoff's Law for Active Dispersions: Shape, Speed, Stroke, and Stress of Swimmers

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In this contribution we will address microscopic (one-body) and macroscopic (many-body) aspects of self-propelled swimmers. We will first present our microscopic analysis [1] of the swimming mechanism of a single illuminated Janus sphere in a near-critical binary solvent. By solving simultaneously for the (coupled) profiles of the temperature, composition, pressure, and flow field in the rest frame of the particle in steady state, we can attribute the motion of the swimmer to body forces at the edge of a micron-sized droplet that nucleates at the hot side of the particle. Next we solve a general formulation of the microswimmer equation of motion with a numerical bead-shell model to calculate the swimming speed, power, and Lighthill efficiency for arbitrary-shaped swimmers and arbitrary strokes. We apply this scheme to a variety swimmers that propel using a rotating helical flagellum [2]. In the final part we will discuss the consequence of the force- and torque-free condition (that any self-propelled particle must obey by Newton's laws) on collective properties of an active dispersion, with a focus on the existence of a well-defined thermodynamic limit, the (osmotic?) pressure [3], and the chemical potential [4] of these out-of-equilibrium systems. This involves the new concept of the swim-potential, and shows the importance of the usually-ignored state of the supporting solvent/medium.

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# A dynamic preferred direction model for the self-organization dynamics of a bacterial microfluidic pump

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A decade ago, Kim and Breuer [1] demonstrated that live bacteria can be successfully used as mechanical actuators in microfabricated fluid systems. They flow-deposit the bacteria (*Serratia marcescens*) to create an active bacterial carpet that can generate local fluid motion inside a microfabricated system. They demonstrate that the bacterial cells in the carpet self-organize and generate a collective fluid motion that can pump fluid autonomously through the microchannel. Moreover, they show that the pumping performance strongly depends on the global geometry of the pump, with narrower channels achieving a higher pumping velocity with a faster rise time.

We model their experiment using the concept of the macroscopic dynamic preferred direction, where the activity is introduced into the system by a symmetry variable that is not static (e.g., nematic director) but is a time rate [2, 3]. In this case it is an axial vector odd under time reversal, corresponding to a collective angular velocity of the bacterial helical flagella. This dynamic ordering variable is coupled to the velocity of the fluid and the system is furthermore subjected to stochastic noise. Mimicking nature, the self-organization is achieved by a feedback mechanism between both fields. A particular challenge is to explain the experimentally observed influence of the pump geometry on the pumping efficiency and coordination time.

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## Light controlled polymer microcrawlers

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Soft robots are machines constructed from flexible materials connected jointlessly, that exert mechanical work by deformation. This is in contrast to the classical 'hard robots' relying on stiff components connected by joints. There are several advantages of soft robots, notably lower requirements on precision during construction and operation which is a significant hurdle for miniaturization of machines in general. Several designs of soft locomotive robots, i.e. crawlers or walkers were reported in the literature[1] and show viability of the concept. However, the mechanisms of wireless control and steering as well as miniaturization below current possibilities of 'hard' robots are yet to be developed.

In this contribution, we describe micro-sized (on the order of 10 to 100  $\mu\text{m}$ ) hydrogel crawlers, remotely controlled and steered by light. The crawlers were prepared using continuous high throughput method Stop-Flow lithography and consist of a thermoresponsive polymer loaded with gold nanoparticles. When irradiated, gold nanoparticles absorb the light and heat up, which leads to local collapse of the thermoresponsive hydrogel. To induce the motion, the rear part of the crawler was irradiated with focused laser pulses, causing periodic contraction and expansion of the irradiated area. The symmetry of the friction between the crawler and the substrate is broken during polymer expansion, which results in forward motion. Laser pulses focused off center enables steering the crawler. While the crawling mechanism is interesting in itself, we also demonstrate the practical application of the developed crawlers, by using them as micromanipulators to transport and assemble other micro objects of comparable sizes ( $\sim 50 \mu\text{m}$ ). The developed system is relatively easy to prepare with high throughput methods, and the motion in terms of coupling between light, temperature, friction and local volume is by a fundamentally new mechanism. Previously presented soft crawler designs were inspired by the motion of organisms (earthworm, caterpillar) [1]. Although our mechanism shares certain features with a caterpillar motion it is unparalleled in living nature, showing that not only bioinspired designs are suitable in soft robotics.

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A fully atomistic modelling of many biophysical and biochemical processes at biologically relevant length- and time-scales is beyond our reach with current computational resources. One approach to overcome this difficulty is the use of multiscale simulation techniques in which different system components are simultaneously modelled at different levels of resolution, these being smoothly coupled together. In the case of biomolecules, functionally relevant parts of the system are modelled at as high a level of detail as necessary, while the remainder of the system is represented using less expensive models. Such a multiscale simulation can employ an Adaptive Resolution Scheme (AdResS) methodology [1], in which the simulation box is divided into atomistic and coarse-grained regions with solvent particles smoothly changing their resolution on-the-fly as they move between regions. Recently, the existing AdResS methodology has been extended to biomolecular systems [2,3]; yet, less attention has been paid so far to the computation of free energies within an AdResS set-up. Here, we demonstrate how the AdResS approach applies to the calculation of thermodynamical properties of biomolecules, and employ it for the first time in combination with Thermodynamic Integration [4] to calculate free-energies.

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# Experimental investigation of a Brownian Gyrator

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Heat engines have been one of the most intriguing research topics in modern thermodynamics owing to their versatility and wide range of applications. Recently, there has been a new-found boost of interest in them following from the advancement of nanotechnology. With the ever-expanding perspectives of micro- and nano-devices, it is interesting to look for ways to realize heat engines at these scales. One such system was theoretically conceptualized recently in the form of a Brownian gyrator<sup>1</sup>. When a Brownian particle is confined in a generic optical potential with two different heat baths acting on it, the asymmetry of the thermal and restoring forces leads to the generation of torques, making it act as a microscopic heat engine. We have shown that indeed it is possible to experimentally realize such a simple microscopic heat engine. We optically trap a Brownian particle in an elliptic potential, and apply different effective temperatures in two orthogonal directions of the trap. We imitate the thermal noise by applying a randomly fluctuating electric field along one direction, thus creating two different heat baths. Under this condition, the Brownian particle exhibits rotational motion, the characteristic properties of which depend upon the strength of the temperature asymmetry along the two directions as well as the angle between potential asymmetry axes and temperature asymmetry axes. We quantify the rotational motion by calculating the generated torque from the experimentally measured particle-trajectories. We show good agreement between theoretical prediction and experimental results.

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# Switching of characteristic motions for swimming oil droplets in concentrated surfactant solution

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The biological and artificial self-propelled micro-objects in viscous medium have attracted the attention of researchers as active swimmer. Among them, a micro-droplet is simple toy model to study their characteristic motion from single droplet level to collective one. Almost previous studied on self-propelled droplets were those at the liquid-air interface or close to the cell bottoms. Recently, some systems where droplets freely swim in three-dimensional space have been reported [1- 4]. One is a dispersion of water droplets in mixture of surfactant and hydrophobic liquids [1, 2] and the other is a dispersion of liquid crystal droplets in an aqueous surfactant solution [1, 3, 4]. In the latter case, the droplets exhibit characteristic curling trajectory originated from the coupling between anisotropy of liquid crystal and Marangoni convective flow [3, 4].

In this study, we have studied the change in self-propelled motion of oil droplets in concentrated aqueous surfactant solutions by varying their sizes. Two types of droplets were used: nematic liquid crystal droplets and dodecane droplets. In both systems, the increase of the droplet size enhances the velocity of droplets and becomes a trigger of switching between different self-propelled modes.

For nematic droplets, with increase of the droplet size, their trajectories gradually change from the helical ones which have been already reported [3, 4] to random curing ones and those look likes figure of “eight”. Their translational velocities monotonous increases with the size. In case of dodecane droplets, surprisingly, they also exhibit curling trajectories at smaller size but becomes circular ones at larger size. We analyzed their trajectory in three-dimensions by using a holographic microscopy and discuss their characteristic motions and their variation with size quantitatively.

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We study highly tunable and switchable active systems of colloidal Janus particles in water. Activity is induced by an AC electric field and can be adapted and switched on and off at will. We can control the speed and direction of the particles by changing the amplitude and frequency of the electric field and the ionic strength of the solvent.

The interplay between activity [1,2], dipolar interactions [2] and electrohydrodynamic effects [3,4] leads to rich behaviour and fascinating dynamics. We observe an active fluid, spontaneously forming rotating clusters and short snake-like chains. Most interestingly, we find giant active clusters that consist of hundreds of active particles. These clusters are partly crystalline, and migrate and continuously rearrange: not only single particles join and leave the clusters, but also the clusters merge or break apart.

We will discuss possible explanations for the fascinating phenomena that we see and discuss our observations in the general context of phase separation and clustering in active systems.

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## Active transport of mucus driven by the self organization of ciliary activity in reconstituted human bronchial epithelium

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Chronic respiratory diseases affect hundreds of millions of people worldwide. They are associated with an impaired mucociliary clearance, which results in a sharp increase in susceptibility to infections and inflammation. Mucociliary clearance is an innate mechanism which provides a continuous protection of the lungs. It consists of a cilia driven collective transport of a protective layer, called mucus, at the surface of the airways epithelium. The mucus, a viscoelastic sticky fluid, traps inhaled particulates, allergens and pathogens and is transported along the airways and out of the lungs.

Despite a rich corpus of clinical studies, chronic respiratory diseases remain poorly understood and quantitative biophysical studies are still missing. We will present the physical mechanisms underlying the mucociliary transport. In particular, we will describe the coupling between ciliary activity, which takes place at the microscopic level, and mucus transport at the macroscopic scale. We will show how the hydrodynamic interactions responsible for ciliary beat coordination/synchronization lead to the formation of active flow patterns and efficient mucus transport at the epithelium surface. These results will be discussed in the context of severe asthma.

# Theory on chemotactic migration of eukaryotic cells

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Eukaryotic chemotactic migration is a ubiquitous kind of cell motility, which plays key roles for developmental processes and the immunological response. Cells perform chemotaxis by intracellular signals that tend to localize at the front or back of the cell according to the guidance cues. It is known that such localization occurs even without extracellular cues, which suggests that isotropy is spontaneously violated in the cellular signal network. In light of this, we established the theoretical model for chemotactic migration of a eukaryotic cell with intrinsic polarity, and studied statistics in cell migration [1,2].

In this poster, I will explain our model and share with you several theoretical results. Our model simulates migration of a chemotactic cell in a chemoattractant solution with the following assumptions:

- The cell spontaneously maintains intrinsic polarity.
- The cell infers the gradient direction by reference to binding states of chemoattractants to receptors on the cell surface.
- The cell tends to reorient the polarity toward the inferred gradient direction. The polarity is also subjected to noise in the intracellular signal process.
- The cell migrates to the polarity direction with a constant speed, so that chemotaxis is realized by bias of the polarity direction due to chemical gradient.

Based on this model, firstly I will discuss statistics in spontaneous migrations of a single chemotacting cell in a uniform chemoattractant solution. The chemoattractant-concentration dependence of the correlation time of migration directions is derived, and the result agrees with the experimental data for *D. discoideum*. We also found that the chemotaxis accuracy is improved by introducing the spontaneous intracellular polarity, that optimally accurate chemotaxis is achieved at an intermediate responsiveness of the polarity to chemical gradient, and that polarized *Dictyostelium* cells adopt such optimal responsiveness [1].

In addition, I plan to explain my recent work in which the theoretical model mentioned above is extended to the multicellular case. Introducing two distinct kinds of cell-cell repulsion interactions into the model, directional ordering and improvement of chemotaxis accuracy in collective migration are investigated.

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## Thermomechanically functionalized rubber

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Liquid crystal elastomers are thermomechanically active materials that couple together elastic properties of elastomers with orientational properties of liquid crystals, a combination through which they exert temperature driven actuation in the form of contraction along the orientational director of their mesogen constituents [1]. Industrial implementation of LCEs has been largely hindered by their geometrical and size limitations which are limited to either macro-sized thin films or to different shaped varieties of nano- or micro-sized LCEs [2,3]. To overcome this problem, we are introducing polymer dispersed liquid crystal elastomers (PDLCEs) as a new thermomechanically functional rubber material. PDLCEs are prepared by freeze-fracturing regular oriented LCEs into microparticles and dispersing them into a polymer matrix. The melt is then then cured under an external magnetic field to align the particles and instill the ensuing order into the specimen. The resulting composite retains the thermomechanical characteristics of LCE inclusions and thus deforms in the same manner. PDLCEs can be processed as a regular rubber material and molded into virtually any shapes or sizes. By sequentially depositing, aligning and curing the pre-polymerized PDLCE melt into a layered material, we can modulate the particle's nematic director throughout the specimen's volume to achieve arbitrary shape changes. Because of the PDLCE's easy synthetization procedure and characteristics, they can be easily enforced into production of future applications in the fields of thermomechanical actuation and additive manufacturing [4,5], while also functioning as a new scientifically interesting soft-soft system.

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We created artificial magnetically actuated microswimmers that swim at low Reynolds numbers. The swimmers are composed of superparamagnetic microspheres that differ in size, causing the asymmetry that is required for successful swimming. If a periodically varying magnetic field is applied, alternating attractive and repulsive forces between the two parts comprising the swimmer appear and the difference in the hydrodynamic drag results in a net translational motion. Depending on the geometry of swimming, we introduce throwers, where a small microsphere is “thrown” by a larger one, and rowers, where a microsphere dumbbell performs a rowing motion. Additionally to the experiments, a numerical simulation was performed that helped us understand the mechanism behind the locomotion and the complex behaviour of the swimmer components.



## Bacterial swimmers in a critical binary mixture

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Bacteria are found to swim and flourish in a multitude of environments ranging from simple aqueous fluids to highly viscoelastic mucus. In this work, we have added *E. coli* into a phase separating binary fluid mixture in order to examine the effect of motile micro-organisms on the processes of phase separation, particularly near the critical point. Using phase contrast microscopy near a glass surface, we image the bacteria and couple differential dynamic microscopy to quantify the fluctuation characteristics of the binary mixture and the near-critical density fluctuations. We observe that swimming *E. coli* bacteria produce a transient trail as they self-propel. By modeling the trail intensity profile, we conclude that it melts diffusively into the fluid, while its lifetime is inversely correlated to the temperature distance from phase separation. By coupling 2D Ising model simulations which conserve magnetization we reproduce the diffusive behavior and we are able to infer the origin of the trail as a local phase reorganization, rather than localized mixing or phase separation. This work on swimming bacteria in binary mixtures paves the way for studies on the effects of active motion on phase transitions.

# Bacteria *E.coli* swimming in high molecular-weight polymers: a universal scaling

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*Escherichia coli* (*E.coli*) has become a model swimmer in the active matter field (e.g. [1]). Numerous studies focus on the swimming in water but bacteria as *E.coli* often live in viscoelastic media such as mucus in intestine tract. Mucus is a strong viscoelastic material with shear-thinning properties containing long polymer chains such as proteins and DNA. Moreover, looking at synthetic active matter in polymers is possible [2] but quite challenging because of the interaction between the fuel and the polymer. Nevertheless, studies on living active matter and synthetic ones in polymer solutions suggest that the exact propulsion mechanism is important to explain the swimming behaviour.

It has been suggested recently [3] that in one polymer, PolyVinylPirrolidone (PVP) high molecular weight (360 kDa) and a coil about 120 nm diameter that small and fast rotating flagella 40 nm thick rotating at 100 Hz create a local high shear rate ( $1 \times 10^4 \text{ s}^{-1}$ ) resulting in a polymer-free channel from its surrounding, while the slow rotating body ( $1 \mu\text{m} \times 2 \mu\text{m}$  rotating at 20 Hz) of the bacterium observe the viscosity of the polymer solution. This is a strong non-Newtonian effect, where bacteria body and flagella observe two different environments.

Here we generalize this study by performing experimental motility measurements of *E.coli* swimming in a lot of different polymer solutions containing large polymer coils: lambda-DNA (Mw=33.10<sup>3</sup> kDa), CarboMetylCellulose (250 kDa, 700 kDa), Polyacrylamide (18.10<sup>3</sup> kDa). These polymers have very different visco-elastic properties. We used high-throughput methods to measure three quantities averaged over 10<sup>4</sup> cells: the mean swimming speed ( $V$ ) and the Brownian diffusion coefficient ( $D$ ) of *E.coli* thanks to Differential Dynamic Microscopy, and the body rotation ( $\Omega$ ) by Dark-Field Flicker Microscopy.

We found that the relevant parameter to explain the nominal values for the swimming speed ( $V$ ) and the body rotation ( $\Omega$ ) in all these polymer solutions at different concentrations is not the bulk viscosity. Indeed, for the same bulk viscosity but in different polymers, one can have a factor 5 difference in  $V$  or in  $\Omega$ . The relevant parameter seems to be the ratio between the viscosity observed by the body and the viscosity observed by the flagella. Thanks to the two environments model [3], we were able to extract this ratio from experimental data and we obtained a good scaling for  $V$  and  $\Omega$  measured in different polymer solutions.

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# Hydrogen-Peroxide-Fuelled Janus Colloids are Active Brownian Particles

10.019

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The fundamental element in the field of *active matter* is the self-propelled particle that transforms free energy from its surroundings into directed motion. These self-propelled particles are commonly modelled as so-called Active Brownian Particles (ABP), where each particle moves with a constant velocity along some instantaneous orientation, which is subject to rotational diffusion.

Up to now only low-order moments such as the mean-square displacement have been used to determine transport properties of self-propelled agents. However, the mean-square displacement of an ABP is insensitive to the shape of the probability distribution, and is, for example, identical to that of a run-and-tumble particle [2]. Therefore low-order moments do not suffice to discriminate between these two transport processes, and a more general spatiotemporal characterization of the particle's dynamics is needed.

Here, we provide an analytic expression of the intermediate scattering function, i.e. the Fourier transform of the probability density, of an ABP in the plane applying a similar solution strategy as in Ref. [1]. We find excellent quantitative agreement between the theoretical predictions and experimental observations from tracking of active colloids propelled by  $\text{H}_2\text{O}_2$  decomposition. Thus, the dynamics of these Janus particles are precisely quantified by the ABP model.

Furthermore, this model provides a good description of ensemble data obtained from differential dynamic microscopy [3], a high-throughput technique that does not require tracking of individual particles. In particular, it permits the extraction of relevant motility parameters and swimming speed distributions of a dilute suspension of Janus colloids. We anticipate that our theoretical results can also be used to investigate the behavior of nanoswimmers using light scattering experiments, and that it may serve as a reference to analyze the onset of collective behavior in dilute systems.

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# Non-Boltzmann stationary distributions and nonequilibrium relations in active baths

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Most natural and engineered processes, such as biomolecular reactions, protein folding, and population dynamics, occur far from equilibrium and therefore cannot be treated within the framework of classical equilibrium thermodynamics. Here we experimentally study how some fundamental thermodynamic quantities and relations are affected by the presence of the nonequilibrium fluctuations associated with an active bath. We show in particular that, as the confinement of the particle increases, the stationary probability distribution of a Brownian particle confined within a harmonic potential becomes non-Boltzmann, featuring a transition from a Gaussian distribution to a heavy-tailed distribution. Because of this, nonequilibrium relations (e.g., the Jarzynski equality and Crooks fluctuation theorem) cannot be applied. We show that these relations can be restored by using the effective potential associated with the stationary probability distribution. We corroborate our experimental findings with theoretical arguments [1].

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We formulate power functional theory [1] for interacting Brownian particles with orientational degrees of freedom [2]. Swimming is induced by an external force field. The framework allows to study active particles in general inhomogeneous and time-dependent nonequilibrium. We prove for steady states that the free power equals half the negative dissipated external work per time, and is hence trivially related to the well-studied average forward swim speed of the particles [3]. The variational theory expresses the free power as a functional of the space- and orientation-dependent microscopic one-body density distribution, as well as of the one-body current, which we split into translational and rotational parts. Minimization of the free power functional with respect to the current(s) yields the physical dynamics of the system. We give a simple approximation for the internal interaction contribution to the total free power (i.e. the excess dissipation functional). In steady states, we evaluate the free power directly using Brownian dynamics simulations for short-ranged soft repulsive spheres. We describe in detail the necessary explicit sampling strategies [4] and show that the theory provides good account of the simulation data.

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Living active matter systems such as bacterial colonies, schools of fish and human crowds, display a wealth of emerging collective and dynamic behaviours as a result of far-from-equilibrium interactions. The dynamics of these systems are better understood and controlled considering their interaction with the environment, which for realistic systems is often highly heterogeneous and disordered. Here, we demonstrate that the presence of spatial disorder can alter the long-term dynamics in a colloidal active matter system, making it switch between gathering and dispersal of individuals. At equilibrium, colloidal particles always gather at the bottom of any attractive potential; however, under non-equilibrium driving forces in a bacterial bath, the colloids disperse if disorder is added to the potential. The depth of the local roughness in the environment regulates the transition between gathering and dispersal of individuals in the active matter system, thus inspiring novel routes for controlling emerging behaviours far from equilibrium. [1]

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## Mechanical and chemical equilibrium in mixtures of active spherical particles: predicting phase behaviour from bulk properties alone

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In equilibrium systems, phase transitions are inherently tied to bulk thermodynamic properties: coexisting phases are in mechanical and chemical equilibrium and therefore have equal pressures and equal chemical potentials. Hence, the bulk properties of the individual phases provide a direct route to constructing phase diagrams. However, for active particles, no such rules exist, and it remains an open question whether their phase behavior can be predicted from bulk (thermodynamic) quantities.

Here, we tackle this pressing question for spherical self-propelled particles, using Brownian dynamics simulations. First, we demonstrate the mechanical and chemical equilibrium of coexisting phases for a binary mixture of attractive self-propelled particles that undergoes a vapour-liquid transition. Mechanical equilibrium is demonstrated by measuring the swim pressure, while chemical equilibrium is shown by bringing each of the coexisting phases into contact with active and passive particle reservoirs separately, and demonstrating that the reservoirs for both phases are identical. We then quantitatively *predict* the phase diagram of a binary mixture of purely repulsive self-propelled particles that undergoes motility induced phase separation, simply by measuring the pressure and reservoir densities of bulk phases and imposing mechanical and chemical equilibrium. We thus show that the phase diagram of active spherical particles can be quantitatively predicted from bulk properties alone. [1]

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## The sound of active liquids

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22 years after the pioneering predictions of Toner and Tu [1], we report the first experimental evidence of sound modes in active liquids and account for their anisotropic propagation.

The collective dynamics of animal flocks was theoretically described in the mid 90's as the fluctuating hydrodynamics of active liquids. From a dual perspective, and fifteen years later, flocking transitions have been reported for a host of man-made motiles systems: from motility assays, to active colloids, to shaken grains. The emergence of collective motion is now well established in synthetic systems. In stark contrast, the fluctuations of the resulting spontaneously flowing liquids remains virtually unexplored. We rectify this situation.

We experimentally demonstrate that the interplay between orientational Goldstone modes and density fluctuations yield propagating sound modes in colloidal flocks, while the underlying dynamics of the active colloids is strongly overdamped. We then exploit these anisotropic fluctuations to infer the constitutive relations of spontaneously-flowing liquids.

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Chemically active swimmers are particles the surfaces of which promote the catalysis of reactant molecules. If the surface properties of these particles are not homogenous, the asymmetry in the number density field generated by the catalysis can lead to particle motion [1, 2]. Accordingly, the dynamics of chemically active swimmers is sensitive to distortions of the density field induced by the presence of other particles as well as obstacles or boundaries. A particularly interesting case is that of chemically active swimmers close to fluid-fluid interfaces. Indeed the fluid interface affects the dynamics of chemically active swimmers by various means. First, it affects the density profile of the reactant and catalytically produced molecules by inducing an inhomogeneity in their transport coefficient. Second, the presence of a fluid interface induces additional boundary conditions that affect the local fluxes responsible for the motion of the particles. Third, the dynamics of a fluid interface can be affected by the local concentration of the solute molecules inducing Marangoni flows. In this contribution we focus on the case of particles *close* to a fluid interface. In such a scenario interface-induced dynamical regimes arise due to both the inhomogeneity of the transport coefficients [3] and the onset of Marangoni flows [4]. Finally, after discussing the single particle cases we briefly analyze collective effects [5].

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# From effective interactions to the interfacial phase behavior and pressure of active particles

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We employ classical density functional theory to study the self-organization in active systems. Using a first-principles approach, we map the self-propulsion onto an effective pair interaction potential, which has been shown [1] to account for the motility-induced phase separation (MIPS) observed for active Brownian particles. We further introduce an effective external potential [2, 3] and define a free energy to investigate inhomogeneous situations. Solely as a result of their activity, we predict [2] that active (Brownian) particles undergo a variety of interfacial phase transitions, e.g., wetting and capillary condensation in purely repulsive systems or drying and capillary evaporation of attractive colloids.

We explain why the effective thermodynamic pressure and interfacial tension do not satisfy the mechanical force-balance condition derived for the present *effective equilibrium* model [3, 4, 5]. Embedding the effective free energy into a more general (dynamical) framework [5], we obtain proper expressions for the mechanical pressure and interfacial tension [5, 6]. Finally, we apply our theory to situations with a non-vanishing particle current [5, 7].

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## Collective motion of cells crawling on a substrate: roles of cell shape and contact inhibition

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Contact inhibition of locomotion (CIL) is the tendency of crawling cells upon contact with other cells to stop their motion or to move away from each other. CIL plays a crucial role for the dynamics of cell colonies, for the process of wound healing, or tumor growth.

We constructed a minimal model for cells crawling on substrates motivated by the cells' internals. The model naturally gives rise to CIL. Despite the simplicity of the model, the cells' collective behavior is highly nontrivial, depending on the shape of cells and whether CIL is enabled or not [1].

We investigated the collective behavior of the cells in bulk, in rings, and the growth of monolayer colonies. The model reproduces typical cell behavior such as the spontaneous coherent motion of keratocytes, or the typical stages of colony growth. We further find that the cells develop density and velocity waves which propagate against the direction of cell migration, similar to the propagation of traffic jams.

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# Dynamics of model bacteria in dense polymer suspensions and networks

10.028

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Swimming bacteria, such as *Helicobacter pylori*, *Pseudomonas aeruginosa* and sperm cells, move through viscoelastic fluids, such as mucus, in vivo. Theoretical models for these complex fluids are typically based on continuum equations which assume a constant density of sufficiently small polymers, homogeneously embedded in a Newtonian fluid. Also experimental studies have mainly focused on dilute and simple polymer solutions. However, real viscoelastic fluids are more structured when considered on the length scale of a microswimmer: they can consist of heterogeneously distributed, up to micrometer long, macromolecules such as mucin polymers.

Here we present results of coarse-grained hydrodynamic simulations of a flagellated bacterium swimming in explicitly modeled macromolecular polymer solutions and cross-linked networks. We find a substantial increase in the bacterium's swimming speed at high polymer density. We discuss the effect of polymer properties such as length, stiffness and cross-linking. We also report the flow fields and the local polymer properties in the vicinity of the bacterium, which can be strongly influenced by its motion.

## ***E. coli* swims faster in tight microtunnels**

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Swimming bacteria exploit viscous drag forces to generate propulsion in low Reynolds number environments. A rotating helical flagellar bundle can propel the cell body at typical speeds of ten body lengths per second. Not surprisingly, this ability to efficiently swim is preserved even in confining micro-environments which constitute their typical habitat. Quantitative studies would require the ability of fabricating complex environments with controlled geometrical properties. Experimental studies so far were limited to large diameter micro capillaries or 2D confinement. In this last case, *E.coli* has been shown to swim with an unaltered speed even when the gap size is slightly larger than the cell body thickness. The case of tight 1D confinement is however more challenging requiring 3D fabrication capabilities. Using two-photon polymerization we fabricate 3D microstructures that can confine swimming bacteria in quasi 1D geometries. We observe individual *E.coli* cells swimming through a sequence of micro-tunnels with progressively decreasing diameters. We demonstrate that *E.coli* motility is preserved also in tight 1D confinement. Moreover we find that there's an optimal channel diameter for which the increase in flagellar thrust due to 1D confinement can even overcome the increased drag on the cell body resulting in swimming speeds that can be up to 15% larger than the bulk speed.

# Hydrodynamics of microswimmers: Phase separation and the influence of gravity

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Active motion of microorganisms and artificial microswimmers is relevant both to real world applications as well as for posing fundamental questions in non-equilibrium statistical physics. Microswimmers are often modelled as active Brownian particles, neglecting hydrodynamic interactions between them. However, real microswimmers, such as ciliated microorganisms, catalytic Janus particles, or active emulsion droplets, employ propulsion mechanisms reliant on hydrodynamics. Therefore, we use the squirmer as a model swimmer and multi-particle collision dynamics [1] to explore the influence of hydrodynamics on their phase behavior in a quasi-two-dimensional geometry [2] and on their motion under gravity.

Building on previous work [3], we examine the influence of hydrodynamic interactions on this motility-induced phase separation. For a range of mean densities and Péclet numbers, we observe how the system decomposes into a dilute and a cluster phase, which then coarsens over time. The most striking difference with the phase diagram of active Brownian particles [4, 5] is that a larger mean density results in a lower density of the coexisting dilute phase, which is a clear signature of hydrodynamics. We explain this by studying the mechanical pressure balance in the system. In addition to active and steric pressure, we need to include a hydrodynamic pressure, which explicitly results from the flow field generated by the squirmers, in order to fulfill pressure balance [2]. Furthermore, we find that pushers or pullers suppress phase separation by increasing the critical Péclet number.

Inspired by experiments [6, 7] and theoretical work [8, 9], we also examine collective dynamics in the presence of gravity. We observe a rich phenomenology, depending not only on the relative strength of gravity but also on the long-range hydrodynamic interactions between swimmers and with the container's walls. A system of dense squirmers exhibits layering followed by a conventional sedimentation profile with superimposed large-scale convection. Under strong gravity and at small densities, single layers of squirmers at the bottom wall form and show interesting structure formation depending on their swimmer type. This includes hydrodynamic Wigner crystals and the formation of swarms.

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Many microorganisms, such as bacteria and algae, possess relatively rigid bodies whereas they generate self-propulsion by using flexible appendages called flagella. Such organisms exhibit many distinctive collective behaviors as a result of the interplay between the self-propulsion and hydrodynamic interaction at various particle concentrations [1]. However, so far most theoretical studies of microswimmers neglect the finite size effects of the cell bodies in the treatment of the hydrodynamic interactions. Hence, they are valid only at low concentrations. Here, we present a minimal model for spherical microswimmers and investigate the role of their finite size on the hydrodynamic interaction among them. We find that the reflected flow from the swimmer surfaces significantly affect the hydrodynamic interactions even at distances considerably larger than the swimmer size. We derive the full mobility matrix that connects the linear and angular velocities of one swimmer to the active and passive forces and torques acting on all the other [2]. We also discuss the implementation of the above long-ranged hydrodynamic interactions in dynamic simulations through the use of the Ewald summation technique.

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# Shape-dependent guidance of active Janus particles by chemically patterned surfaces

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Catalytically active Janus particles in solution create gradients in the chemical composition of the solution along their own surfaces, as well as any nearby confining walls. These interfacial chemical gradients can drive localised surface flows through the molecular interaction between the diffusing chemical species and the surface material. In turn, these surface flows, which include “chemi-osmotic slip” on confining walls and “phoretic slip” on the particle, drive flows in the bulk solution, leading to directed motion of the particle. Notably, chemi-osmotic and self-phoretic contributions to particle self-motility can cooperate (if they drive motion in the same direction) or compete (if they drive motion in opposite directions.)

Since the particle motion ultimately originates in a molecular interaction potential, it is sensitive to the material identity of the bounding surfaces. We consider how to pattern a planar substrate (e.g., by adsorbing two different materials) in order to control the interplay of self-phoresis and chemi-osmosis and thereby guide the motion of active Janus particles. We consider two classes of particle shape: spheres and elongated, rod-like particles, such as ellipsoids and spherocylinders. We develop a set of analytical “point-particle” approximations that show excellent agreement with full numerical calculations for all particles. We find that particle trajectories qualitatively depend on shape. A Janus sphere can “dock” at an interface between two substrate materials: the sphere aligns its axis of symmetry with the interface normal and completely stops moving [1]. Rods, on the other hand, can exhibit both “docking” and “gliding” steady states. In “gliding,” the particle axis is attracted to a steady *oblique* angle with the interface normal, and the rod steadily translates along the interface. Our analytical expressions reveal how the enriched behavior of rod-like particles arises from a shape-dependent sensitivity of particles to various components of the wall-driven flow.

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## Small activity differences drive phase separation in active-passive polymer mixtures

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Recent theoretical studies found that mixtures of active and passive colloidal particles phase separate but only at very high activity ratio [1, 2]. The high value poses serious obstacles for experimental exploration of this phenomenon. Here we show using simulations that when the active and passive particles are *polymers*, the critical activity ratio decreases with the polymer length. This not only facilitates the experiments but also has implications on the DNA organization in living cell nuclei. Entropy production can be used as an accurate indicator of this non-equilibrium phase transition.

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## Multistability in the actin motility assay

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The actin motility assay represents a hallmark experiment for the physics of active matter and was instrumental in exploring and characterising the onset of collective motion and the formation of polar density waves. Yet, the microscopic origin of the observed emergent patterns had remained ambiguous. We demonstrate that a weak perturbation of the microscopic interaction between filaments can drastically alter the symmetry and shape of the emergent patterns, showing a transition towards nematic high-density lanes. Moreover, we find a large region in parameter space that shows multistability: exhibiting polar waves and nematic lanes simultaneously, the system resembles a novel chimera-like state with competing symmetries. We predict that weak microscopic interactions are crucial and facilitate multistability.

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Polymers composed of extensile active elements have symmetry-breaking bending instabilities that lead to motion in the direction opposite to the signed curvature [1, 2] while contractile filaments suppressed transverse perturbations [3]. We study a collection of such polymers confined to interior or surface of a spherical volume. The forces and torques mediated by active flow are explicitly taken into account by adding active hydrodynamic contributions to Langevin equations describing the dynamics of individual polymer. Spontaneous and persistent collective motion in volumetric confinement leads, at moderate polymer densities, to chain entanglement which cannot be released through active reptation. Spontaneous motion in surface confinement leads to athermal production and annihilation of hairpins and disclinations. Our results suggest new active systems that combine aspects of polymeric, colloidal, and liquid crystalline soft matter.

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Active particles achieve spontaneous motion by breaking the symmetry of the surroundings. In addition, in most practical situations, they are influenced by the environment in various manners. Indeed it is an interesting problem how active particles behave as a consequence of the interplay between active motion and passive reaction to external stimuli. For active particles swimming in a fluid environment the external flow field has a crucial effect. To study this effect systematically, the behaviour in a characteristic flow profile, such as a simple linear shear flow, a Poiseuille flow, or a swirl flow, is often investigated. Here we discuss the case of a Poiseuille flow, which appears in a flow channel.

In particular, we are interested in the effect on deformable active particles such as liquid droplets that self-propel due to the Marangoni effect. Based on symmetry considerations, we have derived a set of coupled nonlinear time-evolution equations that models active deformable particles under an external flow field [1]. For simplicity, we consider only the second-mode deformation which represents an elliptical (ellipsoidal in 3d) deformation, and we confine ourselves to a two-dimensional space. From symmetry, the self-propulsion direction of the particles tends to be either parallel or perpendicular direction with respect to the longitudinal axis of the elliptical shape deformation.

In the limit of rigid particles, our equations of motion reduce to those for circular or elliptical rigid active particles that have been studied before [2, 3]. In the previous works, a swinging motion around the centerline of the flow as well as a tumbling motion around the channel wall were observed [2, 3]. When the active particle is deformable, we found that particles self-propelling in the parallel direction to the shape deformation exhibit a swinging motion, whereas those self-propelling perpendicularly show a straight motion along a stream line far from the confinement [4].

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Mechanosensitive channels (MSCs) are oligomeric transmembrane proteins that regulate the osmotic pressure acting on bacterial cellular walls. Under a hypoosmotic shock, the channels open up to form a nanometre-sized pore which allows the non-selective passage of small solutes. Although the crystal structures of MSCs have been thoroughly investigated, the physical mechanisms of gating on biologically relevant time- and length-scales are not well understood yet. Coarse-grained simulations are a unique tool that enable us to study the physics of gating and its dynamics on experimentally accessible scales. We designed a coarse-grained model in which MSCs are described as a series of rod-shaped subunits, and the surrounding lipid bilayer is modelled using a three-beads-per-lipid model. [1] Molecular dynamics simulations accurately reproduced the expansion of a channel subjected to a sudden increase in osmotic pressure. It was revealed that an asymmetric pore opening during gating is preferred over the previously theorised symmetric iris-like expansion. The gating activity was quantified by tracking the net flux of osmolyte particles passing through the open pores. We find that channel design heavily influences the overall gating activity via parameters such as the channel size, number of monomers and the interaction between the individual monomers. The cooperative gating is then addressed. Our results are of importance not only for understanding the mechanisms of mechanical sensing in living organisms, but also for the rational design of artificial mechanical nanosensors..

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Active fluids show a variety of self-sustained non-equilibrium phenomena. An intriguing example is the emergence of a turbulent state in bacterial suspensions, denoted as mesoscale turbulence [1]. In contrast to turbulence in an ordinary fluid, mesoscale turbulence is characterized by the formation of vortex structures exhibiting a typical length scale. Recent publications have shown that a fourth order field theory for the collective microswimmer velocity describes the main features of mesoscale turbulence, including the emergence of the typical vortex size [2, 3]. Such a fourth order continuum theory that couples the polar order parameter of the microswimmers to the solvent velocity can be derived from a microscopic model via the Fokker-Planck equation for the probability distribution [4].

In this work, we extend the theory [4] to include the influence of orienting external fields, such as magnetic fields in the case of magnetotactic bacteria [5] or gravitational fields in the case of gravitactic bacteria [6]. We derive the additional terms in the field equation for the polar order parameter to determine the effects on the state diagram. In addition, we investigate numerically the influence of such external fields on the emerging structures at the transition to mesoscale turbulence.

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For their immense importance and impact on human health and ecology, we aim at understanding the collective behaviour of organisms like sperms, bacteria, and algae in a quiescent environment as well as in the presence of an externally imposed flow similar to microfluidic experiments. These organisms show interesting features as a response to the struggle of surviving in the low-Reynolds flow regime dominated by viscous forces. Surprisingly, bacteria like *B. subtilis* can locally enforce the flow and intermittently turn a smooth parabolic flow to locally plug flow without any clustering [1] or they can intelligently and collectively migrate from regions of low shear to high shear [2]. *Magnetococcus marinus* is a type of bacteria that synthesizes nano-magnets in their cell. When subjected to an external magnetic field as well as an external flow, the local vorticity competes against the tendency of the magnetic bacteria to align along the magnetic field, resulting into formation of 'pearl'-like globules or droplets [3].

Motivated by these experimental results, we numerically study collective dynamics of a large number of squirmer confined in a channel and subjected to Poiseuille flow using multi-particle collision dynamics (MPCD). We build upon our understanding of behaviour of a single microswimmer near the wall and in Poiseuille flow [4, 5]. We first verify the single-squirmers motion of tumbling and swinging trajectories as derived in Ref. [5]. We then conduct a parametric study varying squirmer concentration, swimming speed of the squirmer, and input flow velocity. We measure lateral density profiles, the average squirmer orientation close to the walls and in the bulk excluding the wall regions. These quantities show strong dependence on squirmer concentration and strength of the background flow. Increasing the squirmer concentration while being in Poiseuille flow we see focusing and collective swimming against the flow with a high degree of global polar alignment.

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Active matter refers to out-of-equilibrium systems in which local energy is continuously converted into mechanical work. Examples include all living creatures, from microscopic microorganisms to human beings or larger mammals. It is known that collective motion, which are impossible to predict just by considering the single body dynamics, can be observed in many cases. In particular, in systems of microswimmers, collective motions can arise only due to the hydrodynamic interactions between particles. In this presentation, a numerical work on such collective motions of model microswimmers will be presented. In this work, the squirmer model is employed as the numerical model for microswimmers. [1] In the squirmer model, microswimmers are represented as spherical rigid particles with flowing boundary condition. By changing the value of the swimming parameter, this model can reproduce three different types of microswimmers, namely, pushers, pullers and neutral swimmers; where the flow profile around the swimmer is different depending on the type. Particles propel themselves as a consequence of the reaction to the surface flow. Because the propulsion arises due to the interaction with the ambient fluid, one has to solve the combined dynamics of the particles (squirmers) and the host fluid, in order to adequately describe such squirmer dispersions. As such, in this work, the squirmer dynamics are calculated using a direct numerical simulation method with fully resolved hydrodynamics.

In the case of very localized flow profiles, corresponding to small absolute values of the swimming parameter, it is known that squirmers in bulk tend to align their swimming direction spontaneously. To understand the mechanism for such alignment, we analyzed the binary collision dynamics of the squirmers, by changing the swimming parameter and collision geometry, and investigated to what extent the bulk polar order can be understood in terms of repeated binary collisions. [2] For most cases, at low enough volume fraction, the bulk polar order can be understood by assuming only binary collisions. However, for a specific type of pullers, the ordered state seen in bulk cannot be understood as the result of a series of binary collisions. Furthermore, we have investigated the influence of cylindrical confinement on the polar order formation in the squirmer dispersions. [3] We measured the polar order as a function of pipe size, swimming parameter, and volume fraction. For most cases, the polar order corresponds to that of bulk dispersions at the same volume fraction. However, for a specific range of the pullers, the polar ordering breaks down once the size of the pipe is smaller than some characteristic size. Interestingly, the ranges of the swimming parameter at which we observe such irregular phenomena coincide. We will discuss the possible link between these phenomena in our presentation.

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# Dynamics of epithelial cells in microchannels of varying height:

## Experiments and modelling as active nematic

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We study the short- and long-term flows of Madin-Darby canine kidney (MDCK) cells as they move through microchannels with variable height. When a bottleneck is present, we observe experimentally that flow velocities are higher in the narrow region of the channel. Additionally we find two different types of behaviour as the channel widens: the epithelial sheet either protrudes deep into the unoccupied region or fills up the whole height of the broader section directly.

Similar results are obtained in computer simulations of a biphasic system that combines an active nematic and an isotropic phase [2, 3]. In accordance with the experimental results, flow of the advancing nematic phase is increased inside the tight part of the channel and can produce protrusions as the channel widens. This work builds on previous studies of cell growth in straight channels [1] and will contribute to our understanding of the dynamics of epithelial sheets in complex environments and of tissue invasion.

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# Vapor-Liquid Coexistence and Non-Equilibrium Surface Tension of Active Lennard-Jones Particles

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Active matter represents systems in which the particles are driven due to a continuous energy input. These systems display a variety of novel phenomena like clustering, laning, swarming, not found in systems at equilibrium, but also phase behavior such as condensation, crystallization and phase separation resembling equilibrium systems. Recently, there has been a special interest in extending equilibrium statistical physics concepts such as pressure, temperature and chemical potential to describe non-equilibrium steady states and phase transitions of these systems. In this numerical simulation study we test and extend a few of these concepts to a system of self-propelled Brownian particles interacting via a Lennard-Jones potential in three dimensions at low degree of activity.

Using Brownian Dynamics simulations in an elongated simulation box, we investigate the steady states of gas-liquid phase coexistence of active Lennard-Jones particles with planar interfaces. We chart the vapor-liquid coexistence and show that the coexistence densities are well described by simple power laws. We demonstrate that our out-of-equilibrium system shows deviations from both the law of rectilinear diameters and the law of corresponding states [1]. We then measure the normal and tangential component of the pressure tensor along the direction perpendicular to the interface and verify mechanical equilibrium of the two coexisting phases by using recently obtained theoretical results [2, 3, 4]. In addition, we determine the non-equilibrium interfacial tension by integrating the difference of the normal and tangential component of the pressure tensor, and show that the surface tension as a function of activity is also well-fitted by similar power laws. Finally, we measure the interfacial stiffness using capillary wave theory and equipartition theorem, and find a simple linear relation between the surface tension and interfacial stiffness with a proportionality constant defined by an effective temperature [5].

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## **Topic 11**

# **Biological and Biomimetic Fluids**

## Athermal driven glass like behavior in living cytoplasm

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Mechanics of cells plays crucial roles in many biological processes. Although the viscoelastic properties of cytoskeletons purified and reconstituted in vitro have been intensively studied, the consensus is not yet reached for physical understanding of the mechanics in living cells. Although it is known that wide range of colloidal systems experience jamming or glass transitions by increasing concentration and/or by reducing mechanical loading, the effect of “crowding” with various soft objects, which is furthermore driven out of equilibrium with metabolic activity in cells, are not fully investigated. We therefore investigated the effects of molecular crowding on cellular mechanics by performing microrheology experiments in cell extracts and in living cells.

At first, we prepared several models of cytoplasm which lacks cytoskeletons: three types of cell extracts (*E. coli*, *Xenopus* eggs, and HeLa cells). Viscosity of cell extracts obtained from three different organisms showed similar values and superexponentially increased as the protein concentration becomes higher. The critical concentration  $c^*$  for jamming where viscosity diverges was found to be approximately 0.3 g/ml. 0.3 g/ml is static and physiological concentration in living cells. These observations indicate that the fluidity of cytoplasm is “frozen” at physiological concentrations if there is no metabolic activity.

Furthermore, viscoelastic properties of cytoplasm in the cultured cells (HeLa cells) were measured by performing feedback microrheology with using the embedded probe particles in cells. In feedback-control, output voltage of QPD where a displacement of a probe particle is detected are fed into the “Measure” input of PID controller. Outputs of the controllers are connected 2D-piezo stage respectively. In this study, we performed active/passive microrheology under 3-dimensional feedback of a piezo-mechanical sample stage that enables a probe particle to be stably tracked in vigorous flow as inside of cells.

Glass like behavior in living cells were measured directly with changing the volume fraction of intracellular macromolecules (0.2 ~ 0.6 g/ml) by adding sucrose to the culture media or dilute the culture media and changing the osmotic pressure. Viscosity in living cells showed exponentially increase to concentration of intracellular macromolecules. Of course, kinetics in living cells is not frozen at static and physiological concentration (0.3 g/ml). We speculate the effect of the athermal and spontaneous drive on the out-of-equilibrium mechanics in dense and crowded materials. To observe the effects of athermal forces on crowding components, viscoelastic properties in an ATP depleted cell was measured. ATP in the cell was depleted by adding the NaN<sub>3</sub> and 2-Deoxy-D-Glucose. When ATP is depleted, energy cannot be generated in cells. Mechanics in ATP depleted cell show more elastic behavior than in normal cells. From this difference, it is suggested that athermal forces can fluidize the dense and crowded materials in living cells.

## Supra-folding and unfolding of DNA origamis on polymeric substrates

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DNA origamis are exquisite nanostructures of programmable shapes [1], which can be used as bi- or tridimensional scaffolds to organize guest entities such as particles or proteins [2]. To get exploitable functionality, it is desirable to dynamically control the shape and self-assembly of DNA origami using external stimuli, such as temperature or light [3,4]. In this study, we describe a new mode of origami actuation based on surface interactions rather than heating or chemical modification. We show how layer-by-layer polymeric substrates can be used to induce a supramolecular folding of origamis in a highly controlled fashion. Interestingly, we also show a way to dynamically trigger reversible unfolding into the original origami shape by simple addition of competitors. We quantify the folding/unfolding efficiencies as a function of substrate/competitor characteristics and propose some mechanisms for the supra-folding and unfolding pathways.

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# The flow of a bacterial suspension around a pillar: broken symmetry and biofilm formation

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Across many different habitats bacteria are often found within surface-attached communities known as biofilms [1]. Biofilms greatly enhance bacterial resistance to harsh environmental conditions and antimicrobial treatments, which makes their removal more difficult in industrial and clinical settings. The protection from mechanical and chemical harm is mainly due to the presence of a matrix of extracellular polymeric substances (EPS) secreted by the bacteria, which represents a cohesive polymer network [2] that interconnects biofilm cells. Although bacteria are ubiquitously exposed to liquid flow in natural environments, the human body, and artificial systems, the influence of hydrodynamics on the transport and attachment of bacteria to surfaces and the formation of biofilms remains poorly investigated and understood.

Here, we show that a laminar flow around a pillar can trigger the formation of suspended filamentous biofilm structures known as streamers [3]. We have developed a microfluidic setup that allows the visualization, in real time and at the single-cell level, of the trajectories of swimming cells (such as the human pathogen *Pseudomonas aeruginosa*) around a precisely fabricated microfluidic pillar and the subsequent formation of biofilm streamers. Experiments with pillars of different diameters and with different flow rates allowed us to assess the effect of hydrodynamics on bacterial transport and biofilm formation and to discover with the latter dominated by the interplay between a secondary flow around the pillar and the viscoelastic nature of EPS. In addition, since in this geometry we can study freestanding, single biofilm filaments, we can probe the shear-induced deformation and detachment of bacterial streamers to investigate their intrinsic material properties and viscoelastic nature. We discovered that the formation time and mechanical properties of streamers are strongly related to the diameter of the pillar: streamers form more rapidly around smaller pillars and can withstand stronger hydrodynamic stress before detachment. Understanding the roles of geometry and liquid flow in biofilm initiation offers an opportunity to optimize the design of industrial and medical systems to minimize their formation.

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## Collective dynamics of motile cilia

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Motile cilia are cell organelles able to exert a net force onto a liquid; they are highly conserved across eukaryotes, and enable a variety of functions from the motility of single cell organisms to flow that carries nutrients to our brains. A fascinating process takes place in mammalian airways: a carpet of motile cilia maintains the cell surface free of pathogens and particles by continuously refreshing and clearing a barrier of mucus. In order for this “muco-ciliary clearance” to be effective, cilia motion needs to be phase-locked across significant distances, in the form of a travelling wave, and it is not known how this is achieved.

Our lab is currently approaching this question from two directions: recently we have begun imaging ex-vivo ciliated cell carpets, building on Differential Dynamic Microscopy to quantify the spatial and temporal coherence in the cilia dynamics. On a different scale, we are using Resistive Force Theory to coarse-grain the ciliary beating pattern into parameters of a model system consisting of free-phase driven oscillators coupled via hydrodynamic interactions.

We aim to match the understanding gained from experiments at both many-cilia and single-cilium level with our previous work on such model systems, which showed how hydrodynamic coupling is a mechanism sufficient to establish collective large-scale dynamical patterns.

## Lasers inside live cells

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We have demonstrated a laser completely embedded within a single live cell [1]. The lasers were made out of solid beads or oil droplets. We fed these laser beads to live cells in culture, which eat the lasers within a few hours. The lasers can act as very sensitive sensors, enabling us to better understand cellular processes. For example, we measured the change in the refractive index which is directly related to the concentration of chemical constituents within the cells. Further, lasers were used for cell tagging. Each laser within a cell emits light with a slightly different fingerprint that can be easily detected and used as a bar-code to tag the cell. With careful laser design, up to a trillion cells (1,000,000,000,000) could be uniquely tagged. This would enable to uniquely tag every single cell in the human body, providing the ability to study cell migration including cancer metastasis. Further, by using a micro pipette, we injected a tiny drop of oil containing fluorescent dye into a cell. By analyzing the light emitted by a droplet laser, we can measure that deformation and calculate the tiny forces acting within a cell. Finally, we realized that fat cells already contain lipid droplets that can work as natural lasers [2]. That means each of us already has millions of lasers inside our fat tissue that are just waiting to be activated to produce laser light. The lasers inside cells could be used for unprecedented human-machine interfaces [3] enabling precise imaging [4], diagnosis, better understanding of human body and future applications till now only imaginable in science-fiction.

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## A microtubule dynamics and signaling feedback-loop induced cell self-polarization

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The importance of the intricate interplay between membrane pattern formation, transport along cytoskeletal filaments is now increasingly being recognized. Yet, our understanding of these processes is still highly limited, largely because of the complexity of living of a living cell. Here, first, we propose a bottom-up minimal model combines protein signaling and protein shuttling inside a vesicle, establishing a feedback-loop through signaling protein transports, activation and microtubule dynamics, namely Pak-stathmin-microtubule loops. We then present a novel particle-based simulation tool developed by us, which can efficiently treat the coupling between protein reaction-diffusion and dynamics of filaments. By systematic investigation of this minimal representation of a cell in silico, a self-polarized state with one protein cluster is found, and rich variety of protein pattern and microtubules structures emerge by tuning the signaling magnitude, microtubule density and instability. These theoretical results illustrate how feedback interplay between microtubule dynamics and signaling protein in cell could break symmetry and further direct future experiments in our collaborating group.

## Influence of various buffering agents and excipients on stability of biological drug Pertuzumab in liquid formulation

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Protein-based therapeutics (biological drug or biologic) has found an important place in the pharmaceutical industry due to their effectiveness at low concentrations and less side effects relative to the small molecule drugs.

Protein therapies entered a new era with the influx of a significant number of antibody pharmaceuticals. The number of therapeutic monoclonal antibody in development has increased tremendously over the last 10 years and this trend continues.

However, development of safe and effective antibody pharmaceuticals is not a straightforward process. One of the challenge is development of an optimal drug product formulation assuring long term stability of the biological drug. The main factors that might impact conformational are colloidal or chemical stability of monoclonal antibody in liquid formulations, type of the buffering agent, ionic strength and pH, of the solution.

Pertuzumab is a recombinant humanized monoclonal antibody that targets the extracellular dimerization domain (Subdomain II) of the human epidermal growth factor receptor 2 protein (HER2) and it is used to treat patients with HER2-positive breast cancer.

In general, the initial stage of formulation development process involves use of fast high throughput screening (HTS) methods followed by the more time intense studies on the most promising candidate formulations from HTS.

In case of Pertuzumab formulation development, 84 alternative samples were prepared in 96 deep-well plate. 8 alternative buffers, 3 steric stabilizers and 2 surfactants in alternative combinations were screened using HTS methods. Prepared samples were transferred into 96-well glass and polypropylene tubes and exposed to the temperature, mechanical and freeze/thaw stresses. After treatment, samples were analyzed to monitor degradation product, aggregation and particle formation.

In the next stage, best performing buffers and excipients were further screened at different pH values and buffer concentrations. Samples formulated into glass vials were again exposed to temperature and mechanical stress. In addition to above mentioned methods also oxidation and deamination were monitored.

Performed studies revealed that by the selection of a proper formulation the stability of the Pertuzumab can be improved. Selection of Histidine/HCl or Histidine/Acetate buffer systems leads to the lowest value in aggregation and degradation. The addition of surfactant Polysorbate 20 results in inhibition of particle formation, while Poloxamer 188 showed lower percentage of oxidized protein. In case of steric stabilizer no significant difference was observed between sucrose, trehalose and sorbitol.

# Thermodynamic and structural properties of a simple model for amyloid fibrils.

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Amyloid fibrils are elongated, insoluble protein aggregates deposited in vivo in amyloid diseases. The amyloid-like fibrils are formed in vitro from soluble proteins. The self-assembly of proteins into amyloid-like fibrils is a ubiquitous process that arises for seemingly unrelated amino acid sequences when subjected to the right conditions.

In this presentation we use a two-dimensional coarse-grained model to study equilibrium properties of amyloid fibrils. By Monte Carlo computer simulations we checked phase space and determine what kind of structures are present. At low densities and high temperatures molecules are mostly present as monomers while at low temperatures and higher densities fibrils start to form and then fibrils associate to form higher structures like stack of fibrils. We also estimated free-energies to dissociate proteins from fibrils from the residual concentration of dissolved proteins. Consistent with experiments, the concentration of proteins in solution affects the growth rate of fibrils but not their equilibrium state. Also, studies of the temperature dependence of the equilibrium state can be used to estimate thermodynamic quantities, e.g., heat capacity and entropy.

## Material transport through a binary lamellar stack

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Material transport in living systems is of growing interest in applied fields such as cosmetics and drug delivery systems. A stack of biomembranes is generally considered to play a significant role in transport processes in biological systems.

Previously, it was experimentally shown that the skin permeability coefficient exhibits an Arrhenius type temperature dependence [1]. The permeability coefficient was governed by the diffusion coefficient of solute molecules in membranes, and it increased significantly as the temperature is raised, following the Arrhenius law. On the other hand, it was reported that the self-diffusion rate of sodium ions through unilamellar vesicles increased dramatically near the lipid main transition temperature [2]. In an experimental study by Tayebi *et al.* [3], they reported that a stack of multicomponent lipid bilayers with phase-separated domains exhibits an inter-layer columnar ordering. Such a strong vertical correlation between domains in different membranes can lead to an active material transport mediated through channel proteins that are preferentially incorporated in lipid domains.

To study the material transport through lamellar membranes, we have performed Monte Carlo simulations of binary lamellar stacks with permeants. In our model, multi-layered binary membranes are regarded as a stack of two-dimensional (2D) Ising model in which inter-layer correlations are included [4]. Permeants are transferred to the adjacent layer through vertically connected lipid clusters that are transiently formed by concentration fluctuations in the one-phase region. Concentration fluctuations significantly affect the permeation process especially close to the critical temperature. We show that the permeation rate is an exponentially decaying function of the temperature and the permeant size, whereas the dependence on the characteristic waiting time is described by a stretched exponential function. Our permeation model provides a new aspect for understanding material transport phenomena in multicomponent layered systems.

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## Modeling of the phase equilibria in protein solutions of lysozyme and binary mixture of $\beta - \gamma$ lens crystallins

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The self-assembly of proteins into various structures plays a crucial role in biology. Proteins may self-assemble to form dense liquid phase, crystals, or amorphous aggregates, and an understanding of this process is important for many reasons. The systems of several protein species in water with salts and other co-solvents are often too big to be handled well enough by current explicit-water molecular simulations. As an alternative, many aspects of protein aggregation can be pictured by the coarse-grained DLVO-type of the models with additional anisotropic protein–protein interactions of short range. This strategy was successfully used to model a wide class of globular proteins and to analyze the liquid–liquid phase separation, crystallization, osmotic pressures, distribution of aggregates, percolation threshold, and other physico-chemical properties.

We applied simple models with anisotropic interactions to describe aqueous protein solutions in the presence of low-molecular-mass salts [1] and to analyze the experimentally determined phase diagram of a binary  $\gamma$ D– $\beta$ B1 crystallin mixture [2]. We treat proteins either as a hard spheres or as a hard-sphere dumbbells decorated with attractive sites. We use thermodynamic perturbation theory of Wertheim to calculate the free energy of the solutions and, by applying equilibrium conditions, also the compositions and concentrations of the co-existing phases in the case of the binary mixture. Our model gives accurate liquid–liquid coexistence curves for lysozyme and  $\gamma$  IIIa-crystallin solutions. It provides good fits to the cloud-point curves of lysozyme in buffer–salt mixtures as a function of the type and concentration of salt. It then predicts full coexistence curves, osmotic compressibilities, and second virial coefficients. For the binary mixture of  $\beta - \gamma$  lense crystallins we present complete equilibrium surface in  $T_{cloud}-x_2-\eta$  coordinates and show results for several isotherms, including the tie-lines, as also the temperature–packing fraction curves. Comparison of the model calculations with experimental data shows very good agreement. The present study provided an additional evidence that coarse-grained models can be, in conjunction with the Wertheim’s theory, useful in interpreting experimental data of protein solutions. The model can further be extended to include ions and/or water molecules explicitly.

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# Universal entrainment mechanism controls contact times of freely swimming organisms and passive objects

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Enhanced-diffusion of passive entities by swimming microorganisms has attracted much attention since the seminal work of Wu and Libchaber on the dynamics of passive tracers in baths of bacteria [1]. Most of these studies have been interested in the dynamics of particles that are larger than or comparable to the swimmers. In this case, the colloidal dynamics is generally well-accounted for by persistent random walks. However, the other limit whereby the swimmers are much larger than the tracer particles have been so far overlooked, despite the situation being relevant to numerous important biological and ecological processes such as biogenic mixing, nutrient uptakes, ligand binding, predation by phagotrophs, or virus infection via endocytosis.

Recently we have shown that the dynamics of micron-sized particles in bath of the model puller swimmer *Chlamydomonas reinhardtii* ( $\sim 10\mu\text{m}$  in diameter) is dominated by short range interactions whereby single colloids are entrained in the path of single algae over large distances (up to  $\sim 70\mu\text{m}$ ) [2]. This kind of interaction is rare as the alga has to collide almost head-on with the beads but appears to be essential in order to understand the coarse-grained dynamics of the colloids, well described by a simple jump-diffusion process. In this talk I will first present these results, before moving on to more recent ones on the mechanism of entrainment in itself. Combining experiments with other types of swimmers and numerics with the introduction of our 'outboard' model, we have established that entrainment is a universal feature of the interaction between swimming microorganisms and micrometric objects, only providing that the surface of the swimmer constitutes a no-slip boundary allowing the temporary trapping of the beads. We have found that the competition between Brownian diffusion and advection sets an optimal tracer size (in term of entrainment length or contact time) for any given swimmer (characterized by its speed and size). Finally, using a Taylor's dispersion-like model, we give analytical estimates for the contact time characterizing the swimmer/colloid interaction.

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Ciliary fluid flows play a central role in transferring the microscopic chirality of biomolecules to the macroscopic body asymmetry in embryonic development. Yet the mechanism how this flow is detected is not yet known. In zebrafish, a common model organism in developmental biology, the left-right organizer in which the asymmetry establishment takes place has the form of a spheroidal fluid filled cavity named Kupffer's vesicle (KV). Its walls are lined with beating cilia which establish a rotational flow. There are currently two major competing hypotheses for the detection of this flow and asymmetry establishment. The mechanosensing hypothesis proposes that immotile sensory cilia detect the fluid motion directly. In the alternative chemical hypothesis particles are secreted into the fluid in the centre and the directed flow then leads to a left-right concentration gradient.

We used live confocal imaging to generate 3-d maps of ciliary properties in individual KVs. From these maps we computationally determined the flow patterns and the diffusive propagation of potential signalling particles. The results show that meridional tilt of cilia establishes a robust circular flow in the KV. We used the numerical results to assess the physical viability of the proposed flow sensing mechanisms. We show that relatively low flow velocities with a high local variability preclude direct flow sensing by mechanosensitive cilia. On the other hand, detection of signalling particles subject to directed diffusive transport can provide a robust readout for the establishment of body asymmetry. The work shows that a quantitative analysis of physical limits on flow detection provides insights into the flow detection mechanism that are not yet achievable with molecular methods.

## Optimal multivalent targeting of membranes with many distinct receptors

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Cells can often be recognised by the concentrations of receptors expressed on their surface. For better (targeted drug treatment) or worse (targeted infection by pathogens), it is clearly important to be able to target cells selectively. A good targeting strategy would result in strong binding to cells with the desired receptor profile, and barely to other cells. Using a simple statistical mechanics model, we formulate optimal design rules for multivalent particles that allows them to distinguish target cells based on their receptor profile. We find that:

- 1) contrary to the prevalent paradigm, it is not a good idea to aim for very strong binding between the individual ligands on the guest (delivery vehicle) and the receptors on the host (cell). Rather, one should exploit multivalency: high sensitivity to the receptor composition on the host can be achieved by coating the guest with many ligands that bind only weakly to the receptors on the cell surface,
- 2) the concentration profile of the ligands on the guest should closely match the composition of the cognate membrane-receptors on the target surface and
- 3) irrespective of all details, the effective strength of the ligand-receptor interaction should be of the about of the thermal energy  $k_B T$ . Thus, optimal targeting is achieved when ligands obey “equipartition”: each ligand binds membrane receptors with free energy of  $\approx 1.3k_B T$ . We present simulations that support the theoretical predictions. The design rules we have derived should enable targeted drug delivery with a greatly reduced incidence of side effects.

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# Fluidization of three-dimensional cell sheets by forced rearrangements

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The order-disorder transition in epithelial tissues is often associated with cell mechanical properties such as cell-cell adhesion strength and cortical tension, but it may also depend on cell rearrangements caused by active processes at the cortex level. We find that in intrinsically solid tissues, T1 transformations on cell-cell junctions on average decrease the overall energy if the junction length is below a certain threshold value and increase it otherwise. Based on this, we devise a mechanism where active contractions of the cortex force T1 transformations at randomly chosen cell-cell junctions and fluidize the tissue. We develop a dynamical three-dimensional vertex model to investigate a viscoelastic response of the tissue to an in-plane pure shear deformation and find scaling between the effective tissue viscosity and the rate of forced T1 transformations. Finally, we study shape transformations of compressed tubular epithelial sheets undergoing forced T1 transformations so as to demonstrate the importance of cell rearrangements in determining the final three-dimensional shape of developing tissues as well as their polygonal packing structure.

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Microwaves (MW) are a common type of electromagnetic smog in our everyday lives. They are emitted by various personal electronic devices and household appliances such as cellphones or microwave ovens. MWs are also widely used in chemistry and industry as a source of heat. Water molecules in aqueous solutions align their dipole moments with the oscillating MW field and thus become rotationally excited. This effect also occurs in other polar solvents. A continuous MW irradiation thus creates a non-equilibrium state in which the rotational temperature of polar solvent molecules is significantly higher than their translational temperature.

We performed non-equilibrium molecular dynamics (MD) simulations to study the effect of rotationally excited polar solvent on biological macromolecules, namely a model  $\beta$ -heptapeptide in water and methanol as well as double-stranded DNA dodecamere in water. We ran long MD simulations at increased solvent rotational temperatures ranging from 300 K to 700 K with the GROMOS software. The effects of MWs on the folding behavior of the peptide and on the melting of the DNA duplex were analyzed using RMSD and RMSF values, intramolecular hydrogen bond analysis and cluster analysis. Results show that biological macromolecules remain in their native, more compact state at much higher temperatures when using MW heating in comparison with the conventional heating. This effect is due to the decreased possibility of the formation of long-lasting hydrogen bonds between the biomolecule and the rotationally excited solvent resulting in poorly solvated biomolecules, which compensate for the lost intermolecular interactions by reinforcing their intramolecular interactions.

## Mechano-chemical model for directed processive motility of cytoplasmic dynein

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Linear motor proteins move along their tracks by performing a mechano-chemical cycle in which the conformational and binding affinity changes are coupled to the ATP hydrolysis cycle. Although the two way coupling between the catalytic site, track binding and lever motion is a universal feature of myosins, kinesins and dyneins, the experiments on mutants with one inactive motor head suggest that the dimeric motor could be functional with a less complex mechanism.

Here we will discuss the minimal prerequisites for the dimeric motor to move processively in a directed fashion. Without any coupling between the catalytic site and binding domain, asymmetric unbinding of the trail/lead head and/or asymmetric binding in the forward/backward direction can be driven solely by an asymmetry in the force-induced unbinding rate, together with a conformation dependent internal tension of the dimeric motor. However, the stepping efficiency of such motility is much lower than that of a motor with further allosteric coupling. A more specific and complex mechano-chemical model for cytoplasmic dynein reproduces well the observed stepping efficiency, velocity and force production. By changing the strength of the interhead elastic interaction the model accounts both for uncoordinated and coordinated stepping characteristics of yeast and mammalian dyneins, as observed in recent single-molecule studies.

# Interplay between optical, viscous and elastic forces on an optically trapped Brownian particle immersed in a viscoelastic fluid

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In this work [1], we study the interplay between the different interactions which appear in the Brownian motion of a micron-sized sphere immersed in a viscoelastic fluid measured with optical trapping interferometry [2]. To explore a wide range of viscous, elastic and optical forces, we analyze two different viscoelastic solutions at various concentrations, which provide a dynamic polymeric structure surrounding the Brownian sphere. We study this problem experimentally, using optically trapped microbeads [3] immersed in aqueous solutions of poly(ethylene oxide) or wormlike micelles at different concentrations. Both solutions have been well characterized in the past [4, 5, 6] and display strong viscoelastic properties. Our experiments show that, depending of the fluid, optical forces, even if small, slightly modify the complex modulus at low frequencies. Based on our findings, we propose an alternative methodology to calibrate [7] this kind of experimental set-up when non-Newtonian fluids are used. Understanding the influence of the optical potential is essential for a correct interpretation of the mechanical properties obtained by optically-trapped probe-based studies of biomaterials and living matter [8].

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# Surface-Tension-Based Model of Confined Epithelial Tissues: Buckled Tubular Morphologies

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We theoretically study the shape of single-cell thick epithelial tissues using a model where cells are approximated by adhering liquid drops [1, 2]. We study the effect of apicobasal polarity on a tubular epithelium confined by a rigid tube within a 2D implementation of the model. We first compute the cross-sections corresponding to the global energy minima of the system and characterized by the number of lobes, which generally increase with growing apicobasal differential tension. For small tube radii, we find that transition from the few-lobes regime to the many-lobes regime is discontinuous so that the morphological phase diagram features a critical point terminating the transition. We further analyze the effect of dynamics on the systems, focusing on the interplay between the two processes that induce buckling: Apicobasal polarity and the rate of cellular division [3]. The results are compared to the predictions of other models as well as to experimentally observed tubular epithelia in, e.g., the developing chick gut.

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