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BOOK OF ABSTRACTS

ORAL PRESENTATIONS

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Contents

Plenary Lectures 2
PL1. Johan Martens
PL2. Daniela Kraft
PL3. Jessica Rosenholm
PL4. Michal Borkovec
PL5. Overbeek Medal: Ishi Talmon
PL6. Solvay Prize: Nikolai Denkov
Keynote and Oral presentations 9
Biological and Biologically Inspired Systems
Catalysis and Surface Reactions
Colloidal Gels & Network Structures
Colloidal Stability & Shelf Life
Colloids in Medicine & Controlled Release
Design & Production of Colloids & Nanoparticles
Emulsions, Pickering Emulsions & Foams
Experimental Techniques
Imaging, Scattering & Microstructure
Microdroplets, Microbubbles & Microfluidics
Rheology of Colloidal Systems, Surfactants and Polymers
Self Assembly & Supramolecular Systems
Surface Forces and Thin Liquid Films
Special Session: Nano-ions & Self Assembly
Special session: Wetting & Transport

Author Index

240

Plenary Lectures

PL1. Johan Martens	. 3
PL2. Daniela Kraft	. 4
PL3. Jessica Rosenholm	. 5
PL4. Michal Borkovec	. 6
PL5. Overbeek Medal: Ishi Talmon	. 7
PL6. Solvay Prize: Nikolai Denkov	. 8

Mastering colloids and interfaces: key to innovation in a convergent research model

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Research in the fields of energy, environment, water and human health currently is too much disconnected, which is suboptimal since all rely on very similar physicochemical concepts and research approaches at the molecular scale and they could benefit from shared scientific knowledge. Current inter- and transdisciplinary collaboration of mono-disciplinary experts meets with some success, but such collaboration is slow and may be insufficient to solve the global problems humanity is faced with.

Convergence is a new paradigm proposed in 2011 by MIT [1] and later adopted by the NSF USA, moving beyond the current inter- and transdisciplinary collaboration models, as it proposes truly transdisciplinary integration of Life & Health, Physics & Chemistry, Engineering Sciences to accelerate technological progress in challenging areas of concern to mankind, like sustainable energy, food, climate, health and water."

In the talk a new initiative at KU Leuven, the "Convergent Research Fund' fostering the convergent research idea is presented. Knowledge on how molecules organize themselves at interfaces, how they are transported through membranes and pores, and adsorbed and converted on catalysts is gained from advanced Nuclear Magnetic Resonance spectroscopy. The first successes of convergent research at KU Leuven are presented: in sustainable energy, the development of hydrogen panels, trapping water from atmospheric air and converting it to hydrogen and oxygen gas using solar energy, in chemical manufacturing, altering water properties by hydrophobic interaction to make it less polar and fit for dissolving organic molecules to replace organic solvents; in the field of food production, original concepts for off flavor abatement in aquaculture and fish farming are presented, and in the pharmaceutical area, enhanced bioavailability of poorly soluble drugs by using silica-based drug delivery. It will be explained how the activities are being expanded to the biomedical area.

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Flexible colloidal structures

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Many functional (bio-)molecules possess structural flexibility which provides functional properties and a more complex phase behavior. For example, different conformations may enhance or inhibit a protein's activity in allosteric regulation or enable the catalytic activity of enzymes. Colloidal structures currently lack this property, restricting their use as building blocks in reconfigurable materials and model systems. In this talk, I will introduce colloidal particles with surface-mobile DNA linkers [1,2] – so called colloidal joints [3]- that enable the formation of strong and specific hinging bonds. I will describe how this bond mobility affects their diffusive and self-assembly behavior and demonstrate the assembly of a variety of flexible structures. In particular, I will discuss the formation of colloidal molecules with tunable flexibility and shape in high-yields. These novel colloidal building blocks give access to a new class of materials with great potential in shape-shifting systems, actuators and colloidal robots.

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Mesoporous silica designs tailored for nanomedicine

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One of the main objectives in the development of nanomedicines is to obtain delivery platforms for efficient and targeted delivery of drugs and/or imaging agents to improve therapeutic efficacy, reduce side effects and increase diagnostic sensitivity. A material class that has been recognized for its controllable properties on many levels, which could facilitate the development of such systems, is mesoporous silica nanoparticles (MSNs). Associated traits behind this success are the modularity combined with the vast surface functionalization approaches adoptable for MSNs. Here, the chemical, structural, and textural robustness of the architecture of this inorganic material platform can be readily fine-tuned with the aid of responsive, biocompatible and flexible organic modifications to form multifunctional hybrid materials (Figure 1). Moreover, the four distinct domains that can be independently functionalized,^[1] i.e. the silica framework, the particle surface, the pore walls, and the inner space in the case of hollow MSNs; endows this platform with especially flexible design possibilities.



Figure 1: Using inorganic porous nanoparticles as a platform for further modification allows for a multitude of functions to be incorporated for a vast array of applications within nanomedicine.

Silica is also the most widely used coating for other inorganic nanoparticles, since it is biocompatible, allows for easy further functionalization, and efficiently protects the core material. If the cores are coated with mesoporous silica, the porous shell can also be utilized for incorporation of active molecules such as drugs or molecular imaging agents, creating e.g. multimodal fluorescent-magnetic nanocomposites.^[2] Inorganic nanostructures are readily utilized as biomedical imaging probes due to their inherent detectability by a variety of different imaging modalities, e.g. nanodiamonds for optical imaging^[3] and superparamagnetic iron oxides, SPIONs, for magnetic resonance imaging (MRI). These materials are thus frequently coated with porous or non-porous silica layers in the design of multifunctional core-shell materials.

This Plenary Lecture will outline design aspects that emphasize the utilization of MSNs as a versatile platform for nanomedicine development, covering the whole range from materials design and formulation with different active agents, to *in vitro* cellular evaluations and *in vivo* therapeutic delivery and detection.

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Colloidal Forces

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Numerous phenomena are governed by forces between colloidal particles. Examples include stability of colloidal suspensions, their rheology, or formation of colloidal crystals. The importance of such interaction forces has been appreciated for a long time, but accurate measurements of such forces remained a considerable challenge until quite recently. Presently, however, various techniques are becoming available for direct force measurements. In my view, the colloidal probe technique based on the atomic force microscope (AFM) is emerging as the most promising and versatile one.

The present talk will discuss the use of this technique to measure forces between colloidal particles in aqueous systems. In particular, I will demonstrate that interactions between similar as well as dissimilar particles are principally controlled by electrostatic double-layer and van der Waals forces as already suggested by the classical theory of Derjaguin, Landau, Verwey and Overbeek (DLVO). The talk will further highlight the nature of forces acting between charged colloidal particles in the presence of multivalent ions and polyelectrolytes. While forces in these systems remain DLVO-like and are mainly controlled by charge reversal, additional attractive non-DLVO forces come into play. Additionally, two novel phenomena will be highlighted as well. First, charge regulation effects can become very important for dissimilar particles. Second, double layer forces can become strongly non-exponential in the presence of multivalent coions or like-charged polyelectrolytes.

Cryo-EM of Complex Liquids: A Brief History and the State-of-the-Technology

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It is well accepted in modern science and technology that direct-imaging on the supra-molecular scale is an essential part of full nanostructural characterization of any material system, including complex (nanostructured) liquids. For the latter, the main established tools are cryogenic-temperature transmission electron microscopy (cryo-TEM) and cryogenic-temperature scanning electron microscopy (cryo-TEM). Both techniques, referred to jointly as cryo-EM, involve ultra-fast cooling of the specimen, and its examination at cryogenic temperatures. That makes the specimens compatible with the microscopes, and arrests all perceptible motion during imaging. Another challenge is keeping the temperature and composition of the studied system unaltered during specimen preparation, until it is thermally fixed.

Cryo-EM has its roots in the late 1970s. Over the years many scientists and technologists contributed to the development of specimen preparation, improving the microscopes, improving imaging, and understanding the physics and chemistry of electron beam-specimen interaction. All that has led to better preservation of the specimens during preparation, transfer into the EM, and imaging, improved image resolution, and extension of the application of the methodology to a very wide range of the studied systems, from synthetic to biological, from the aqueous to the nonaqueous, even to systems based on strong acids.

In will start my presentation with a brief history of cryo-EM, especially as applied in the study of complex liquids. Then I will describe and demonstrate some the state-of-the-technology features of cryo-TEM and cryo-SEM that have made very strong impact on the field in recent years. In the last part of the talk I will present recent applications of modern cryo-EM in nano- and biotechnology.

New approaches for surfactant control of foam and emulsion properties

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We have revealed that individual surfactants and their mixtures with other surfactants, polymers and/or particles can be used as powerful active agents for intelligent control of foam and emulsion properties. Four new approaches will be presented as case studies: (1) We showed that two different mechanisms, bulk gelation and Pickering stabilization, can be used for production of ceramic porous materials, with excellent thermal and mechanical properties, from foamed suspensions. These mechanisms lead to materials with different structure and properties, e.g. with open or closed pores. This approach can be applied to different types of solid particles by selecting appropriate surfactants. (2) We showed that one could use cosurfactants of different chain-lengths, various cationic polymers and counterions to modify the kinetics of surfactant adsorption, surface viscoelasticity, bubble-bubble attraction and the related foamability and foam rheological properties of the surfactant solutions. These studies have important implications for the home and personal care formulations. (3) We studied systematically a large series of natural surfactants, called "saponins", which have high surface activity and are used industrially as foamers and emulsifiers. Various plant extracts were compared and wide diversity of surface properties was observed - some saponins exhibit extremely high surface viscoelasticity, while others have other beneficial properties. We showed that the high surface viscoelasticity of the triterpenoid saponins (which differ from the steroid ones) is due to strong hydrogen bonding between the sugar residues of the adsorbed saponin molecules and to tight packing of the rigid hydrophobic scaffolds of these molecules in their adsorption layers. These properties are very different from those of the conventional surfactants. (4) In collaboration with colleagues from the University of Cambridge, UK, we have observed and explained a range of unexpected and non-trivial phenomena in cooled alkane-inwater emulsions, including spontaneous drop self-shaping and drop self-bursting when the alkane drops undergo liquid-to-solid phase transition. Although the mechanisms of these fascinating phenomena are still debated, we have demonstrated how one could use and/or combine different long-chain surfactants to push the system into different desired scenarios.





Figure 1: Examples of spontaneously formed oil drops with flagella obtained via cooling of (a) C_{15} -in-water and (b) C_{16} -in-water emulsions, stabilized by $C_{16}EO_{20}$ nonionic surfactant (Brij 58).

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Keynote and Oral presentations

Biological and Biologically Inspired Systems
Keynotes
BIO1 13
BIO2 16
BIO3 21
Catalysis and Surface Reactions
Keynote
CAT1
Colloidal Gels & Network Structures
Keynotes
GEL1
GEL2
GEL3
Colloidal Stability & Shelf Life
Keynotes
STAB1
STAB1
Colloids in Medicine & Controlled Release 57
Keynotes
MED1
MED2
MED3
MED4
Design & Production of Colloids & Nanoparticles
Keynotes
DES1
DES2
DES3
Emulsions, Pickering Emulsions & Foams
Keynotes
EMUL1
EMUL2
EMUL3
Experimental Techniques
Keynotes

EXP1 \ldots \ldots \ldots 11^4
$EXP2 \dots \dots \dots \dots \dots \dots \dots \dots \dots $
Imaging, Scattering & Microstructure
Keynotes
IMAG1 \ldots \ldots \ldots \ldots 12^4
IMAG1
IMAG2 13
Microdroplets, Microbubbles & Microfluidics
Keynote
$DROP1 \dots \dots \dots \dots \dots \dots \dots \dots \dots $
DROP2
Rheology of Colloidal Systems, Surfactants and Polymers
Keynotes
RHEO1
RHEO2
RHEO3
Self Assembly & Supramolecular Systems
Keynotes
SELF1
SELF2
SELF3
SELF4
SELF5
SELF6
Surface Forces and Thin Liquid Films
Keynotes
SURF1
SURF2
SURF3
Special Session: Nano-ions & Self Assembly
Keynotes
ION1
ION2
ION3
ION4
Special session: Wetting & Transport
Keynotes
WET1
WET2
WET3
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Amorphous Magnesium-Calcium-Phosphate nanoparticles: effect of pH, Mg²⁺ and complex fluids on their formation and crystallization

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Recent investigations showed that the secretion of calcium and phosphate ions from humans' distal small intestine into the lumen leads to the formation of Amorphous Magnesium-substituted Calcium Phosphate nanostructures (AMCPs), which trap macromolecules, such as antigens and bacterial peptidoglycan, and transport them to the immune cells of the intestinal tissue [1]. The formation mechanism and the factors affecting AMCPs' stability are thus relevant topics, as a deeper understanding would clarify the role of these newly-discovered particles and the potential pathological implications. As amorphous calcium phosphates are highly unstable [2], it is important to contextualize AMCP formation and stability in conditions compatible with the gut and to understand which are the key parameters that affect its features in biologically-relevant media. In this contribution, we describe the effect of pH and Mg²⁺ concentration on the stability of endogenous-like AMCPs [3]. The crystallization of the amorphous phase in different conditions was investigated by combining Infrared Spectroscopy and X-rays Diffraction, while the morphology and the nanostructure were assessed by means of Electron Microscopy. We found that both pH and Mg²⁺, tightly controlled at the gut level, influence the lifetime of the amorphous phase and the nature of the formed crystalline material. In the attempt of making a step towards the in vivo conditions, we synthesized AMCPs in a commercial simulated intestinal fluid, which contains sodium taurocholate and lecithin [4]. The influence of their self-assembly on the formation of AMCPs was investigated, as well as their effect on the particles' nanostructure and stability. The formation of AMCP in the presence of proteins, such as the hydrogel-forming mucins abundant in the intestine, will also be presented. As a next step, the interactions of AMCP with gut microbiota and mycobiota will be addressed, so to contribute to unravel the role and biological function of this intriguing nanomineral.



Figure 1: sketch representing AMCP formation and features in simulated intestinal fluids.

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The impact of non-equilibrium conditions in lung surfactant membranes

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The bio-membranes making up the major barriers of the human body are all made of lipids and proteins, which separate a dry outside from the water-rich tissue of our insides. This difference in water subjects the membrane to non-equilibrium conditions as water is driven from our body creating composition gradients throughout the membrane. These gradients affect the structural organization as well as the functional properties, yet it is a problem often omitted. We have studied a particularly important bio-membrane, the lung surfactant film, under these nonequilibrium conditions. The lung surfactant film covers the inside of the alveoli and ensures the proper function of our lungs. Deficiency of this membrane may cause respiratory distress syndromes, which may be lethal if left untreated^[1]. In the treatment of pre-maturely born children, a lung surfactant extract can be supplied to the baby^[2]. We have used such a clinical lung surfactant extract in a novel millifluidic capillary set-up^[3] to reconstitute bio-membranes at the air-water interface and evaluate their structure and composition under non-equilibrium conditions. With the combination of X-ray scattering and Raman microscopy we observe both composition and structural gradients. In addition to the water gradient in the membrane we also observe the build-up of both lipid and protein gradients, which results in structures that are not observed under equilibrium conditions.

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Calcium-magnesium phosphates: from the physico-chemical study to the preparation of functional materials

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Calcium and magnesium-based phosphates are essential components of the human body, since they contribute to maintain its structure and guarantee the proper functioning. Crystalline calcium phosphate (CaP) is the main mineral component of natural bone and teeth, where it is present as non-stoichiometric hydroxyapatite in bones, or as carbonated hydroxyapatite, in the mature enamel of teeth [1]. On the other hand, amorphous CaP-based structures are frequently employed by Nature to build up biologically strategic components, such as calciprotein particles in the blood or casein micelles in maternal milk [2]. Moreover, it has been recently found that endogenous nanoparticles of amorphous calcium and magnesium phosphate (AMCP) in intestine act as chaperones in the transport of macromolecules, such as bacterial peptidoglycan, to the immune cells of intestinal tissue [3]. Each specific environment of the human body clearly has a crucial role in guiding the formation of different phosphate species, including the presence of specific biological macromolecules. All the experimental data highlight that these features are affected by both chemical affinity and confinement effects [4], suggesting new strategies towards the design and preparation of functional materials based on calcium-magnesium phosphates. This contribution summarizes the results obtained in the last few years in our group on this topic. Case-studies will be presented in order to cover the most significant aspects, highlighting that a synergistic approach including physico-chemistry and material science is the most effective strategy for the preparation of biologically relevant functional materials. The formation of hydroxyapatites in a biocompatible composite will be discussed as an example of mineralization templated by complex fluids [5]. The investigation on the formation and stability of synthetic intestinal AMCP nanoparticles will be presented [6,7]. Finally, examples of magnesium phosphate bone cements will be presented, especially focusing on the material properties and the applicative aspects [8].

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Protein-like dynamical transition in microgels: the role of water-macromolecule coupling

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Hydrated proteins become biologically active above a temperature of about 220 K at which also a sudden increase of the protein mobility occurs. This molecular process, known as the protein dynamical transition, consists in the onset of anharmonic motions which allow proteins to explore conformational states of functional relevance. Thus it has been the subject of intensive research, but a deep understanding of its nature still remains elusive.

Evidence of a protein-like dynamical transition was recently reported also for a non-biological system, such as poly(N-isopropylacrylamide), PNIPAM, microgels. ^[1] These micrometer particles, made of a cross-linked polymer network, are widely investigated as smart materials due to their stimuli-responsive behavior. However, PNIPAM microgels share many features with proteins, because of their extended covalent connectivity and their amphipilic character.

In this contribution we describe the molecular origin of the low temperature dynamical transition in microgels, as obtained from atomistic molecular dynamics simulations.^[2] The study is based on a nanoscale model of microgel network in water (Figure 1) which has been validated with a direct comparison with elastic incoherent neutron scattering experiments.^[1] We show which molecular processes control the dynamics of both the macromolecule and water below the dynamical transition temperature. Through a comparison with the low temperature behavior of bulk water, we demonstrate that below the dynamical transition temperature water dynamics is mainly determined by the macromolecule-water hydrogen bonding interaction. Our findings suggest that the macromolecule-water coupling plays a driving role in the dynamical transition. Therefore this phenomenology should be a general feature of hydrated macromolecular systems able to form hydrogen bonding interactions with water.



Figure 1: Atomistic model of PNIPAM microgel network.

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Self-association of intrinsically disordered proteins

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Intrinsically disordered proteins (IDPs) have, despite the structure function paradigm, proven to be functional. In addition, their lack of structure can be related to their function. ^[1,2] While many IDPs are monomeric, some are prone to self-associate or aggregate, which can be of importance for the functionality or in some cases connected to disease. Our aim is to understand what controls self-association of IDPs and how it affects IDP behavior, by assessing the balance of interactions in a self-associating IDP system and characterize the formed micelles. As a model system we use the saliva protein Statherin, which self-associates in solution in a protein concentration dependent manner, ^[3] see Figure 1. Since Statherin is also known to adsorb to the tooth enamel, we are interested in the effect of self-association on both bulk behavior and adsorption to surfaces. We use a combined approach of experiments and simulations, where the simulations aid in interpretation of the experimental results and provide additional insight on a molecular level. By small angle X-ray scattering (SAXS) and coarse-grained simulations we have studied the response to protein concentration, temperature, salt, and urea, which shows that the self-association is hydrophobically driven, while electrostatic repulsion represses the growth of micelles. In addition, increased temperature counteracts self-association, as shown in Figure 1, which based on simulations is suggested to be mostly an entropic effect. Furthermore, we perform ongoing studies on the adsorption to silica, using ellipsometry and quartz crystal microbalance with dissipation. Preliminary results point towards a strong correlation between self-association and adsorbed amount.



Figure 1: Average association number determined by SAXS versus protein concentration at different temperatures, pH 8, 20 mM Tris and 150 mM NaCl.

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An investigation of dendrimer-like DNA: theory and experiment

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Dendrimers are synthetic macromolecules, characterized by a highly branched and regular internal architecture. Recently, dendrimer-like DNAs (DL-DNAs) were synthesized via enzymatic ligation of Y-shaped DNA building blocks. These charged dendrimers represent a novel macro-molecular aggregate, which holds high promise in bringing about targeted self-assembly of soft-matter systems in the bulk and at interfaces.

We present a joint simulational-experimental study of these novel macromolecules. Based on a bead-spring model for the DL-DNAs (of varying generation numbers) we perform large-scale simulations to determine the equilibrium properties and the conformational characteristics of these macromolecules. The obtained results are compared to light scattering experiments ^[1]. The simulation data provide a broad variety of additional information about the internal molecular structure of DL-DNAs by varying the generation number and the salinity of the solvent. In an effort to simulate concentrated solutions of DL-DNAs, we extract an effective, coarse-grained potential, based on Widom's particle-insertion method. With this potential at hand, we investigate the bulk behaviour of DL-DNAs. These findings are essential to investigate if these dendrimer systems are viable candidates for the experimental realization of cluster crystals with multiple site occupancy in the bulk ^[2].



Figure 1: simulation snapshots of G1, G3, and G6 DL-DNA (from left to right). Different generations of the dendrimers are indicated by different shades of blue, while counter-ions are colored red.

The study of these charged dendrimer systems represents a relevant field of research in the area of soft matter due to their potential role for various interdisciplinary applications, ranging from molecular cages for drug delivery to the development of dendrimer- and dendron-based ultra-thin films in the area of nanotechnology ^[3].

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pH-responsive mimetic bacterial membranes: The role of cardiolipins

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Figure 1: Monolayer at the air-water interface.

Cardiolipin (CL) is a phospholipid commonly found in mammalian and bacterial membranes.^[1] Whilst its role in mammalian cells has been widely studied, its role in bacteria membranes remains inadequately understood.^[2] A challenge for combatting gram-negative bacteria arises from the robustness of its asymmetric double membrane structure.^[3] Here, as a first step, we perform an XRR study of mixed lipid layers as a basic mimicry of the inner leaflet of the outer membrane of gram-negative bacteria.

Our goal is to understand on a fundamental level how cardiolipins affect the selfassembly, stability, and elasticity of bacterial membranes. First, we studied monolayers with various PE, PG, and CL compositions spreading at the air-water interface using a Langmuir-Blodgett trough under different pH solutions (1.3, 5.1 and 12.1) (Figure 1). Synchrotron XRR profiles at the air-water interface (Figure 2) showed the thickness and structure of the mixed monolayers depended on the pH of the subphase due to the presense of Cardiolipin. This yielded

information on the structure of the inner leaflet of the outer bacterial membrane. Secondly, supported bilayers were formed by rupturing of mixed liposomes containing PE, PG, and CL on a mica surface. The corresponding XRR profiles from the supported bilayers suggest Cardiolipin that has an effect on the structural integrity mixed of membrane.



Figure 2: XRR profiles of DOPE: DOPG: CL (80:15:5) at air-water with different pH of subphase.

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Improved Phospholipid Lubrication by Prevention of Hemifusion

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Phospholipids (PL), particularly phosphatidylcholines (PC), have been proved as boundary lubricants which greatly reduce friction between surfaces coated by PC vesicles or bilayers. It is believed to underlie the remarkable lubrication of articular cartilage in synovial joints, where the friction coefficients are 0.03~0.001 under physiologically high pressures of 2~10 MPa.^[1] The origin of superlubrication by PL is hydration lubrication, where the slip-plane lies between two highly hydrated phospholipid headgroup surfaces.^[2] Hemifusion occurs between two PL bilayers under certain conditions, such as defects on the bilayer, mismatch of different lipids,^[3] resulting in disappearance of the headgroup headgroup slip-plane and hence breakdown of the lubrication.

In this study, we aim at improving the lubrication performance of PL mixtures modified surface by preventing hemifusion. Surface force balance (SFB), a cutting-edge and high-precision technology to measure surface forces, has been used to measure the normal and shear forces between two surfaces coated with PL bilayers/vesicles under aqueous conditions. A vesicle fusion method was utilized to modify the substrate (mica) and different configurations of PC lipids (one in gel state, and the other in liquid-crystalline state) and negatively charged PL-SUVs mimicking those identified in synovial fluids were investigated.

The results show that there is an interplay between the phase-state of the lipids and their charge, which can be manipulated to achieve better lubrication.

In conclusion, improved lubrication has been achieved by selective adsorption of gelstate neutral PC or by attaching negatively charged boundary lubricants to the substrate via divalent cations.

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Biological and Biologically Inspired Systems Understanding the role of lipoteichoic acid in Gram-positive bacteria membranes

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Lipoteichoic acid (LTA) tethered to lipid membrane (Fig. 1A) of Gram-positive bacteria is identified as a facilitator for biofilm formation, leading to bacterial adhesion and infections.^[1] Driven by its amphiphilic nature (Fig.1B), the interaction of LTA with lipid constituents in bacteria membrane has important implications to the lipid packing and membrane integrity.



Figure 1 : Location (A) and structure (B) of lipoteichoic acid (LTA) in Bacillus subtilis membrane

In this scenario, *Bacillus subtilis*, a Gram-positive bacteria contains LTA as a major constituent in the periplasm. ^[2,3] We have examined the role of LTA in perturbing the structure of mixed lipid monolayers with compositions mimicking those of bacteria species. The variations in packing density of the mixed lipid monolayer film were analyzed by measuring the Langmuir isotherm for various lipid compositions comprising 1,2-dipalmitoyl-sn-glycero-3-phospho-(1'rac-glycerol) (DPPG), 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine (DPPE), Cardiolipin (C16:0) and LTA. The experiments were performed at different temperatures and subphase pH to understand their effects on the lipid packing. *In-situ* X-ray reflectivity (XRR) measurements at different surface pressures for a mixed lipid composition revealed the variations in surface roughness, film thickness and lipid packing density caused by LTA at different mole fractions in mixed lipid composition. The atomic force microscopy (AFM) measurements revealed changes in the surface topography and roughness caused by LTA. We suggest LTA incorporated within mixed lipid monolayers is an essential structural constituent for designing a Gram-positive membrane mimic.

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Cells grab onto particles – novel hybrid hydrogels with improved mechanical and micro-rheological properties

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Bio-interfaces have been at the forefront of biologically relevant research since the first report of their influence on cell adhesion^[1]. Hydrogels are perfect candidates for biointerfaces, but they typically suffer from structural weakness.

In this work, we have developed a novel type of hydrogels using thermal annealing accompanied with addition of calcium carbonate particles for improving their mechanical properties. Such hydrogels will be also attractive due to a possibility of functionalization of their surfaces with enzymes^[2]. We have further studied mechanical and micro-rheological properties by AFM, while cryo-SEM and Raman were also used in our studies. Morphology of hydrogels and calcium carbonate particles is changed by the annealing process; the mesh size of the hydrogels is found to be from 0.3 μ m till 5 μ m, while the size range of particles is from 0.1 μ m till 8 μ m. Mechanical values for gels ranged from 191 kPa to 1.2 MPa.

Subsequently, the developed hydrogels have been tested for pre-osteoblast cell adhesion revealing that materials developed in this work effectively promote cell adhesion, and this is related to mechanical properties of hydrogels with vaterite particles.

But the nature of cell adhesion is quite intriguing - we have found that cells adhere to hydrogels by grabbing exactly on the sites of particles. Points of adhesion of cells on the hydrogel surface were accurately determined with the nanoscale resolution by AFM (Figure 1).

The novel hydrogels developed in this work with improved mechanical and rheological properties will be excellent bio-interfaces. ^[3]



Figure 1. Photo scanned using AFM area and fluorescence microscopy.

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How Osmolytes Modulate Lipid Interactions

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To counteract environmental stress, many organisms regulate the amounts of molecularly small solutes termed osmolytes. Recent evidences show that osmolytes alter lipid homeostasis, with potential consequences to cardiovascular disease.[1] Although it is known that many osmolytes exert an apparent attractive or repulsive force between self-assembled lipid membranes, all proposed models fail to fully account for the origin of this force. Toward resolving the mechanism by which osmolytes modulate lipid interactions, we followed several osmolytes, including urea and TMAO and their interaction with lipid membranes in agueous solution.[2] We found that TMAO pushes adjacent membranes closer together, while urea makes membranes grow further apart. By contrast, our newly formulated methodologies for determining membrane elasticity from simulations[3,4] show almost no change in membrane structural and material properties in presence of TMAO or urea. Experiments and simulations further show that the change in the force between membranes is due to the partitioning of TMAO away from the volume between bilayers. This in turn stems from the exclusion of TMAO from the lipid-water interface. Hence, the underlying mechanism resembles protein stabilization by osmolytes. By contrast urea is equally partitioned in lipid and bulk, and its action is related to modified van der Waals interations. We extend our conclusions to address additional biologically relevant solutes (e.g., sugars, DMSO and urea), explaining how osmolytes can increase membrane-membrane attraction or repulsion depending on their preferential interactions with lipids. Finally, we discuss the potential synergistic role of osmolytes acting together in the modifications of lipid adhesion and fusion interactions.

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Microfluidic manipulation of biomaterials mechanical properties via thermophoresis

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The optimisation of the interactions between cells and the material over which they are cultivated is important for tissue engineering and biomedical applications such as tissue repair and wound healing. Biomaterials exhibiting a gradient of mechanical properties can be used to regulate cell behaviour which is dependent upon the elasticity of the substrate^[1,2]. However, the possibility to create these materials is still limited especially at the micron scale^[3].

By carefully imposing and controlling temperature gradients across a microfluidic channel and exploiting thermophoresis^[4,5], we demonstrated here the generation of gradients of Young's modulus in a biocompatible hydrogel ^[6]. A microfluidic device consisting of a main microchannel and two side channels acting as hot and cold thermal sources ^[7] are used to apply the transversal temperature gradient and fabricate biocompatible gellan gum hydrogels exhibiting stiffness gradient (Figure 1a-b). Moreover, we effectively control the stiffness gradient of the biomaterials by regulating the temperature difference across the device and altering the concentration of the polysaccharide. We characterised the biomaterials by evaluating locally the Young's modulus by AFM nanoindentation across the 600 µm width of the hydrogels, obtaining values ranging from 20 to 100 kPa, and gradients of up to 130 kPa/mm (Figure 1c). Scanning Electron Microscopy (SEM) images showed a gradient of porosity and a more compact structure at the stiffer side, corresponding to the side exposed to the lower temperature, demonstrating that gellan gum molecules drifted towards the colder side and hence present a positive thermophoretic behaviour. Furthermore, we monitored the cell behaviour over time by seeding MC3T3 osteoblasts on the surface of the biomaterial. Cell viability, migration and mineralisation are observed via fluorescence microscopy and X-ray fluorescence (XRF) on the surface of the material at different stiffness areas and time points for up to 30 days.



Figure 1: (a) schematic of the microfluidic device used to impose a temperature gradient and thermophoresis principle showing accumulation towards the cold or hot side depending on the sign of the Soret coefficient (ST); (b) photograph of an actual device; (c) typical exponential distribution of the Young's modulus along the width of the biocompatible concentration gradient material as measured by AFM.

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Beyond a Carrier: Monoolein core-filled liposomes as a multifunctional tool for cancer theranostics

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Nanocarrier-based chemotherapy is one of the few nanotechnology-based therapies that reached the clinics and many liposomal drug formulations are currently available in the market. Despite several liposomal formulations were already proposed for the delivery of the anticancer drug doxorubicin (DOX), the majority uses "active loading" methods. The "active loading" methods are used to increase DOX amounts in the nanocarriers but have however the disadvantage of drug precipitation and formation of dimers for which the therapeutic value is yet to be proved [1].

In this work it is proposed an innovative nanocarrier system of DODAB:MO(1:2) that has previously been studied for its great potentiality of encapsulating drugs, not only at the DODAB bilayer level, but also at the inverted non-lamellar MO-enriched phases at the vesicle interior[2]. EE studies revealed high encapsulation values of DOX turning the developed formulation in a very promising nanocarrier system for DOX. The biophysical effects of DOX in the formulation indicated an increase in the cooperativity of the phase transition confirming DOX homogeneous distribution at the membrane level. The nanocarrier system has also demonstrated adequate sizes for cellular uptake and EPR effect, as well as a pH dependency that favours drug release in low pH cancer tissue. The delivery of the anticancer drug was also evaluated in cancer cell models showing intracellular distribution of DOX after using 3D confocal microscopy. The colocalization of DOX inside the nucleus is seen in Hoechst labeled cells and in addition FLIM is used to identify the DNA intercalation of DOX that is associated to fluorescence lifetime change of the drug. Cytotoxicity assays concluded that DOX encapsulated in DODAB:MO (1:2) has a better cytostatic effect than the free drug, confirming the potentiality of the developed formulation to be used in cancer treatment.

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Dual-Responsive Photocatalytic Polymer Nanogels

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Selective activation of photocatalysts under constant light conditions has recently been targeted to produce multi-responsive systems. However, controlled activation, with easy recovery of the photocatalysts, induced by external stimuli remains a major challenge. Mimicking the responsibilities of biological systems by multiple triggers can offer a promising solution. Herein, we report dual-responsive polymer photocatalysts in form of nanogels consisting of a cross-linked poly-N-isopropylacrylamide nanogel, copolymerised with a photocatalytically active monomer. Dual-responsive polymer nanogels undergo a stark reduction in diameter with an increase in temperature, above the lower critical solution temperature, shielding photocatalytic sites retarding activity. Temperature-dependent photocatalytic formation of the enzyme cofactor nicotinamide adenine dinucleotide (NAD+) in water demonstrates the ability to switch on/off photocatalysis. Moreover, photocatalysis of fine chemicals (benzaldehyde, benzyl-1-phenylmethanimine and 1,2-dioctyldisulfane) has been conducted in the nanogels swollen state, demonstrating the utility of the designed material.



Figure 1: Dual-responsive photocatalysts that can be selectively switched on or off as a function of temperature. Inclusion of photocatalytic units into a thermo-responsive nanogel matrix, which allows selective photocatalysis at low temperature in the swollen state but not at elevated temperatures in the contracted state.

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Straining nanoparticles affects catalytic activity Ger Koper¹



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We report^[1] on the effect of lattice strain in three different types of core–shell electrocatalyst particles on their catalytic activity towards the oxygen reduction reaction. We decouple the changes in catalytic activity with respect to a geometrical and an energetic contribution, both of electronic origin.

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Surface modified Ga-silicates catalysts prepared via the aerosol process

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Background. The production of biodiesel as an alternative to fossil fuels yields approximately 10wt% of glycerol as by-product. A promising route for its valorization is represented by the condensation of glycerol with acetone into solketal. A sustainable way to perform this reaction envisages the use of heterogeneous catalysts displaying both Brønsted and Lewis acid sites. Porous silicates presenting a metal inserted as single site in the framework can be active and selective catalysts for this reaction.^[1]

Aim. In this work, the role played by the hydrophobic/ hydrophilic balance of the catalyst surface will be investigated. A series of Ga-silicate catalysts with different degrees of methylation were synthesized via the aerosol process and tested in the acetalization of glycerol with acetone to produce solketal.

Methods. Methyl-functionalized Ga-silicates were synthesized via the aerosol process from a mixture of TEOS and methyltriethoxysilane using $Ga(NO_3)_3$ as Ga precursor. Three degrees of functionalization have been selected: 5, 10 and 15 mol%. Pluronic® P123 or F127 was used as templating agent.

Results. The aerosol process allowed to synthesize a series of methylated Ga-silicates. The solids were characterized by N₂ physisorption, XRD, TEM and ICP-OES spectroscopy. The successful incorporation of Ga as single site within the silica framework was assessed via ⁷¹Ga Solid State NMR and XPS spectroscopy. These mesoporous Ga-silicates showed excellent catalytic performance in the conversion of glycerol into solketal under solventless conditions and the best catalyst displayed outstanding turnover number and selectivity. A positive influence of the methylation on the performances the catalysts was observed. Furthermore, it was observed that even a very low degree of methylation was effective to enhance the catalytic performance of the materials.

Conclusion. A series of methylated Ga-silicates was successfully synthesized and tested in the valorization of glycerol. The best catalyst displayed high turnover number, evidencing the positive influence of surface functionalization. (Figure 1)



Figure 1: TEM micrograph of methylated Ga-silicate (left) and solid state magic angle spinning (MAS) ²⁹Si NMR spectra of the synthesized materials (right)

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Topochemical engineering of bioaerogel beads for advanced applications in photocatalysis

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Topochemical engineering is a method of designing the fractionation (disassembly) and fabrication (assembly) of highly engineered functional materials using a combination of molecular and supramolecular techniques¹. Bioaerogel beads are spherical and porous and can be highly engineered to be used as catalyst support material. This type of catalysts is cost-effective and suitable for multiple re-usage and has been rarely explored in cellulose reaction research. In this work, NiFe-layered double hydroxide (LDH) was tailor-made in situ on anionic cellulose beads to form a hybrid, supported photocatalyst for the first time (Figure 1). The hybrid beads were prepared in a size larger than the pulp fibers in order to make the catalysis reaction heterogeneous in nature. Hydrophilic pulp fibers were converted into hydrophobic pulp by photocatalytic topochemical grafting of ethyl acrylate using the LDH-cellulose bead catalyst². The approach identified for the modification of the pulp fibers is the "hydrogen abstraction-UV photografting" because the low-energy, UV radiation-induced grafting offers advantages, such as a reduced degradation of the backbone polymer and a control over the grafting reaction. After grafting, the pulp fibers showed increased water repellency and unaltered thermal stability, indicating the hydrophobic, plasticizing nature of the pulp, which in turn accounts for its thermoformable behavior. These acrylated pulp fibers can be further designed/customized for waterproof or oil absorption applications in packaging and personal care products.



Figure 1: Cellulose beads (CB) oxidized with TEMPO to generate anionic CB (ACB). NiFe-LDH was assembled on the surfaces of ACB to form hybrid beads (HB). The HB was used for photocalytic topochemical grafting of ethylacrylate to pulp fibres leading to a hydrophobic polysaccharide-based material.

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Catalysis sydewifanesBroentiextraction understood from a colloidal model CAT1-5

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Liquid-liquid (or solvent) extraction is the most commonly used method to recycle and separate metal ions from highly concentrated aqueous solutions. In most cases, known two extractants dissolved in a solvent are used in the synergistic ratio, but the understanding of the phenomena behind is still unclear. Currently, mainly the first neighbor supramolecular complexation term is considered, but this does not provide an explanation in the micellization threshold and synergy observed [1,2,3].

In solvent extraction, the self-assembly of amphiphilic molecules into the organized structure is the phenomenon responsible for the transfer. We propose a colloidal model of spherical micelles (aggregates) in the dilute regime for the prediction of extraction efficiency, and for the self-assembly in the complex fluid. The model describes a mixture of non-ionic and acidic extractants showing synergistic character. It is based on establishing the free energy contributions of the spherical aggregate formation in the organic phase. The leading complexation, reduction of accessible volume for ions and water molecules, weak self-assembly of extractants, bending of the extractant film, extractant head group interaction, are *e.g.* taken into account.



Figure: Synergetic valley for Europium extraction

Contrary to the current paradigm of simple stoichiometry behind liquid-liquid extraction, there is a severe polydispersity of aggregates completely different in compositions, but similar in the free energy. Mapping the polydispersity of self-assembled aggregates rationalizes the fraction of the synergy peak in metal cation extraction due to the formation of mixed and pure extractant inverse micelles. The global overview of the complex nature of synergistic mixture shows different regimes in self-assembly, and thus in the extraction efficiency which can be finely tuned with respect to the green chemistry aspect.

This work [4] disentangles quantitatively the interplay between chelating and ion-exchange amphiphilic molecules combined in reverse micelles that are the basis of most efficient extracting processes.

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Pickering Emulsions (PEs) are emulsions stabilized by particles that adsorb at the oil water interface and prevent coalescence of the droplets^[1]. The aim of the current work is to use PEs as a reaction environment for catalytically activated reactions for example for the hydroformylation of 1-dodecene^[2]. The expensive and water-soluble Rh-catalyst is retained in the water phase while the oil phase can be separated via filtration using the high stability of PEs^[3]. It was found that a positively charged particle surface increases the particle-catalystinteraction. This leads to an increase in the reaction conversion^[4]. The aim of the present study is to explain this effect and to investigate the processes occurring at the interface in general. As a first approach, differently modified particles including silica and polystyrene nanospheres are used to stabilize PEs. The intended differences in surface charge, hydrophobicity and their natural differences in size and material as well as the interaction with the Rh-catalyst are quantified by Transmission Electron Microscopy (TEM), Atomic Force Microscopy, Dynamic Light Scattering and Sessile Drop Contact Angle Measurements and the influence on their surfaceactive behavior in PEs is studied by Fluorescence (FM) and Optical Microscopy. The measurements show that modified silica spheres represent a suitable reference system for the investigation of the influence of distinguished particle properties on macroscopic PE properties.



Figure 1: A TEM Image of the modified silica nanospheres (SNS), B Fluorescence microscopy image of (SNS) stabilized PE (water phase dyed with fluorescein), C Decrease of ζ -potential of positive Polystyrene Spheres with increasing catalyst concentration shows catalyst particle interaction

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Colloidal gel elasticity arises from the packing of locally glassy clusters

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In colloidal gels, attractive interactions among suspended colloids drive a thermodynamic instability that promotes aggregation, arresting in a space spanning network structure possessing unique mechanical properties. Gels are ubiquitous in industrial processes and products where fine solids are dispersed in polymer solutions, including agrochemicals, consumer care products, and pharmaceuticals. In applications, the rheology of a gel is its principle material property of interest, including its elasticity and yielding. We use a recent model depletion gel that enables the rheology, structure, and particle interactions to be measured in concert [1]. As the attractive strength between particles increases, the gel elastic modulus increases, but that this change cannot be accounted for by the immediate increase in bond stiffness between particles and particle clusters alone derived from the depletion interaction energy. Here, the quantitative agreement between integrated experimental, computational, and graph theoretic approaches are used to understand the arrested state and the origins of the gel elastic response. The microstructural source of elasticity is identified by the I-balanced graph partition of the gels into minimally interconnected clusters that act as rigid, load bearing units. The number density of cluster-cluster connections grows with increasing attraction, and explains the emergence of elasticity in the network through the classic Cauchy-Born theory [2,3]. Clusters are amorphous and iso-static. The internal cluster concentration maps onto the known attractive glass line of sticky colloids at low attraction strengths and extends it to higher strengths and lower particle volume fractions.



Figure 1: Simulated gel microstructure and underlying clusters identified by graph theory.

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 Colloidal Gels & Network Structures
 GEL2-1 Keynote

 Microgel based surface coatings and free standing responsive membranes

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Smart surface coatings are of interest for divers applications such as sensors[1], anti-fouling coatings [2], drug delievery [3] and cell culture substrates [4]. For the latter, coatings made of thermoresponsive Poly-(*N*-isopropylacrylamide) pNIPAm microgels have been found to allow reversible switching of cell adhesion upon heating and cooling [3-5]. Microgels react extremely fast upon changes in temperature or pressure and in some cases the volume change occurs within 2 ms [6].

The present contribution presents our recent results related to the use of microgels as surface coatings and the extension of these works towards preparation of free standing membranes from cross-linkable microgels. The approach is based on the deposition of microgels, containing cross-linkable comonomers and subsequent irradiation either with electrons or light.

Monolayers of such copolymer microgels were spin-coated onto a silicon-wafer covered with a polyelectrolyte. Atomic force microscopy (AFM) was used to study the surface coverage, topography and the thickness of the coatings. Fig. 1 (left) shows a cross-linked microgel sheet. Such sheets are macroscopic (in the square cm range) and can be transferred to Si-Nitride chips for the use in electrochemical cells. We are able to show that such membranes can be used to thermally regulated e.g. ion flux.





Figure 1: Left: AFM image of an electron beam cross-linked microgel based membrane. Right: Macroscopic membrane transferred to a silicon nitride chip with funnel hole for conductivity measurements

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Multi-scale relaxation in aging gels: from localized plastic events to system-spanning "quakes"

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Relaxation of internal stresses through a cascade of microscopic restructuring events is the hallmark of many materials, ranging from amorphous solids like glasses and gels to geological structures subjected to a persistent external load. By means of Photon Correlation Imaging (PCI), a recently developed technique blending the powers of scattering and imaging, we provide a spatially and temporally resolved survey of the restructuring and aging processes that spontaneously occur in physical gels originating from arrested phase separation^[1]. We show that the temporal dynamics is characterized by an intermittent sequence of spatially--localized "microquakes" that eventually lead to global rearrangements occurring at a rate that scales with the gel age. Notably, these dramatic upheavals of the gel structure are heralded by a progressive acceleration of the microscopic gel dynamics that originates from recognizable active spots and then spread at a large but finite speed through the gel (see Figure 1). Within the 'slack' phase between two of these `macro--quakes', the fluctuations of the degree of temporal correlation obey a non-Gaussian statistics described by a generalized logistic distribution. The evidence we obtained suggests a strong connection both with the stress relaxation processes taking place in earthquake sequences and with recently proposed self-organized oscillator mechanisms of crystal plasticity.



Figure 1: Sequence of PCI "correlation maps showing the time development of a "quake-like" decorrelation event in a colloidal gel.

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Stress Transmission in Colloidal Gels

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Understanding transmission of stresses in colloidal gels is crucial to unravel the origin of gel collapse, design colloidal networks with superior mechanical properties and therefore increase the shelf life of commercial products. In this study, arrested emulsion gels were prepared by mixing frictionless colloidal PDMS emulsions with non-absorbing polymers hydroxyethyl cellulose (HEC) which introduce depletion attractions between oil droplets^[1]. Particle-resolved study by confocal microscopy was performed on these emulsion gels where oil droplets were fluorescently labelled. Compared with bulk oil droplets, higher fluorescent intensity were detected where oil droplets are in contact with each other, i.e. there is a normal force between these two droplets^[2]. From confocal images, we extropolated the size of contact area that were proportional to the magnitude of forces, according to Princern force model^[3]. Force chains in colloidal gels were also identified. Unlike granular systems, where an exponential decay at large forces were commonly observed, we found a Gaussian decay at large forces in arrested gels^[4]. We also performed local structural analysis using Topological Cluster Classification (TCC) and packing anaysis to characterise the gel system.

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Morphology and rheology of sheared colloidal gels dispersed in a viscoelastic matrix

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The balance between hydrodynamic and interparticle forces determines the microstructure of colloidal dispersions and their rheology. In a viscoelastic suspending medium, the occurrence of normal stress differences in particular has shown to affect the hydrodynamic forces acting on single particles and aggregates. In the present study, the role of a viscoelastic medium was investigated experimentally by studying weakly aggregated PMMA particles of 1 µm diameter in PDMS at volume fractions near the percolation threshold. Viscoelasticity was introduced by means of branched PDMS. A cone-partitioned plate geometry was used to measure the magnitude and sign of first and second normal stress differences, and subsequently derive information on the pair distribution function. Additionally, a fast high-resolution rheo-confocal setup was employed to monitor both the microstructure and the rheological behavior simultaneously. On one hand, by performing stress jump experiments, viscous and elastic stress contributions stemming from the different components could be analyzed as a function of the medium viscoelasticity. On the other hand, by means of the high speed confocal microscope, using counter-rotating plates and structured illumination optics, we could study the structural evolution during steady state and transient flows at the flow-vorticity plane over a wide array of length scales. The complementary measurements reveal the formation of dense particle aggregates, tumbling as a whole and orienting in the vorticity direction, as expected for attractive particles. The main effect of the viscoelastic matrix is the densification of these clusters, which affects the effective volume occupied by the particles. The latter affects the steady state stresses, but also the long-term diffusivity and recovery of the microstructure. Overall, it can be concluded that changing the viscoelasticity of the matrix affects network morphology as well as the storage modulus of a colloidal gel.
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The ability to control the assembly of spherical colloidal particles into specific geometries is fundamental for the development of new materials. Generally, the inter-particle interaction is chosen as the control parameter. In this way, a short-range attractive interaction, normally due to depletion interactions, promotes particle aggregation and gelation is only found as the result of irreversible spinodal decomposition. However, the presence of a long-range repulsive interaction due to electrostatics can limit the growth of the clusters, while controlling their morphology. While the role of the balance between attraction and repulsion to observe different microstructure states has been widely documented ^[1,2], their rheological behavior remains largely uninvestigated.

In this contribution, we address this problem by means of non-equilibrium molecular dynamics (NEMD) simulations on a wide variety of clustered states under steady shear. We show that the competition between attraction and repulsion can influence the stress-strain relationship ^[3]. Furthermore, we observe how the clusters evolve during the deformation of the system caused by the shear flow. In the studied cases, we find that the stress overshoot follows a power-law dependence on the Péclet number, similarly to previous reports for depletion-induced^[4] gels. Remarkably we find that the power-law exponent depends on the employed colloid-colloid interactions. We connect this exponent to the fractal dimensions of the clusters in equilibrium and shear, showing that shear deformation can be used as a further tool to modify in a controlled way the morphology of the aggregates in the system.



Figure 1: Evolution under steady shear of the radius of gyration of the clusters interacting with (a) shortrange attraction only and (b) with an additional long-range repulsion as a function of strain. Lines provide reference slopes of the different fractal dimensions.

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Modelling attractive networks under shear using MD simulations

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In rheology, computational experiments are an important addition to laboratory experiments. They deliver complete particle-level observables and can probe length and time scales not accessible by traditional experimental techniques. Thus, they can yield insights into phenomena such as creaming, sedimentation and aggregation in suspensions.

Many simulations have used pressure driven flows to simulate the feedback between structure and flow in colloidal systems. However, for shear flow – which more closely matches rheological experiments – no reference implementations are available. Some implementations force the colloidal particles or fluid onto a linear shear profile. Hence, they do not take slip or shear banding, especially in poorly stabilised systems, into account properly. The Lees-Edwards (LE) boundary conditions [1] are a suitable and physically consistent method to generate a shear flow in a molecular system and allows one to study the non-linear rheology of colloidal systems. We recently implemented LE in the molecular dynamics software package ESPResSo [2] and have now applied them to a system of particles undergoing an attractive interaction. These systems are of special interest for e.g. industrial applications because they can mimic effects regularly experienced during processing and application of insufficiently stabilized particles. Furthermore, attractive forces, namely capillary forces can be used to generate a sample spanning network [3], which can be used for stabilization purposes.

Here, we demonstrate influences of continuous shear during the buildup and breakdown of a particle network and measure viscoelastic properties using oscillatory shear. Hydrodynamics can be included via lattice Boltzmann techniques or dissipative particle dynamics. A special focus will be put on the online analysis of stresses, hydrodynamics, and cluster structures as well as their impact on flow phenomena. Furthermore, we show that it is not sufficient to solely investigate parameters like the fractal dimension or the coordination number.

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Fast self-healable metallo-gels with mixed ionic-electronic conductivity

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The development of self-healing materials opens perspectives to fabricate devices with unprecedented lifetimes and recyclability that can be integrated with flexible electronics. However, the timescale at which these materials operate remains a significant challenge to overcome. This article describes the fast self-healing behavior of aluminum/iron polyphosphate metallo-gels and their hybrids with polyaniline and gives a detailed investigation of their electrical responses. The samples can be cut, molded and healed by manual handling. The rebuilding process is mediated by water uptake and was directly observed by environmental scanning electron microscopy. Metallo-gels with and without polyaniline can be mixed to give homogeneous samples, where the conducting polymer is uniformly distributed within the inorganic matrix. Cyclic voltammetry experiments showed that polyaniline behaves within the metallo-gel in the same manner as it does in aqueous electrolytes. Furthermore, polyaniline adds electronic conductivity to the originally ion-conducting polyphosphate metallo-gel, as demonstrated by impedance spectroscopy. The ionic and electronic conductivities are 1.3-1.7×10⁻² S cm⁻¹ and 5.2×10⁻⁴ S cm⁻¹, respectively. Such properties result from the "free" and "bound" water within the hydrogel network and the dynamic nature of the aluminum-phosphate interactions within the supramolecular system. The features presented here make these materials good candidates to be used as moldable electroactive binders in carbon-based electrodes and all-solid-state flexible separators for repairable electrochemical capacitors and batteries.

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Figure 1: Self-healing in Al/Fe-polyphosphate metallo-gels. The transparent film (a) was cut in five pieces (b) with a knife, then shaped by manual handling (c, d), healed into a single part (e), formed into a cube (f), and finally pressed to restore its original shape.

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Relation between structure and dynamics in homogeneously and heterogeneously crosslinked PNIPAM microgels

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Thermoresponsive poly(N-isopropylacrylamide) microgel particles have been largely studied in the past due to their interesting fundamental properties as well as their potential for application in drug delivery, sensor technology or biotechnology. In this contribution, microgel particles with homogeneous and heterogeneous crosslink distribution and different crosslinker concentrations will be studied with small angle neutron scattering (SANS) and neutron spin echo spectroscopy (NSE) [1].

The segmental dynamics of polymer chains in solution, as described by the Zimm model, is modified in microgels due to the presence of crosslinks and the crowded environment inside the particle, both inducing heterogeneities, for example "frozen" inhomogeneities or density fluctuations. Such structural heterogeneities have an impact on the segmental chain dynamics, which makes NSE, the highest resolution neutron spectroscopy technique, the experiment of choice for accessing variations and changes induced by changes in crosslink distribution and crosslink density.

A short outlook on interface effects on the internal structure and inhomogeneities of microgel particles will be given [2].

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Colloidal Gels & Network Structures GEL2-4 Study of particulate migration during silica-latex colloidal film formations

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Colloidal coatings have been used extensively to achieve specific surface properties like hydrophobicity^[1], flame retardancy^[2], self-cleaning^[3] and others. As the presence of small proportion of such particulate deposition can alter the properties of materials significantly, it is therefore important to understand the mechanism of migration of particles affecting their spatial location during the film formation process^[4], and especially the interplay between binder and the surface chemistry of the particles. One of such particles of interest is colloidal silica which has been used widely for enhancement of surface area, magnetic and optical properties of the substrates, among others^[5]. Often these silica particles are used in combination with other polymeric moieties, surfactants or binders for specific applications.

In this study an attempt was made to understand the silica and binder particle migration during the film forming process. Factors governing the mobility and passage of binder and silica particles were evaluated with respect to particle concentration and drying rate. Effect of silica surface chemistry, as well as nature of the binder, on the arrangement behaviour was also explored in detail. It was found that polymer infiltration, particle stratification, peclet number and the size ratios of play a significant role in determining the surface morphology and spatial location of constituent particles. A suitable selection of these parameters can help achieve desired surface functionality by altering the deposition of type of particulates on the top surface. Hence, this study has the aim to set a fundamental background to the assembly of various particulate systems for industrial coating applications.



Figure 1: Schematic describing development and regulation of surface features and functionalities

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Sugar-triggered emulsion stability using responsive microgels

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Microgels are soft and deformable particles. When constituted with amphiphilic chains like poly(*N*-isopropylacrylamide) (pNIPAM), they adsorb at liquid interfaces. Soft microgels were found to efficiently stabilize Pickering emulsions [1] or foam films [2] in good solvent conditions. These emulsions could be destabilized on demand upon collapse of the microgels by heating them above their volume phase transition. Softness is a key requirement for emulsion stability, as it controls the extent of microgel spreading and interfacial elasticity [3]. Moreover, softer microgels adsorb with a faster kinetics at liquid interfaces [4].

In this work, we investigate sugar-responsive microgels as Pickering emulsions stabilizers. Microgels having a sugar-dependent swelling were synthesized and characterized by means of AFM, TEM, DLS and Zeta potential. The stability of the resulting emulsions was also examined both at rest and under applied stimuli. In the absence of sugar, the microgels were found to behave as rigid spheres. The resulting emulsions were mechanically fragile. Upon sugar addition, the microgels swelled and became softer, allowing highly stable emulsions. The stabilization mechanisms were explained in light of complementary experiments on model interfaces, regarding spontaneous adsorption kinetics and Langmuir film compression studies. The role of microgel functionalization and deformability is discussed.



Figure 1: Sugar-dependence of microgel swelling and consequences on the resulting emulsion stability.

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Synthesis and characterization of hollow adhesive silica nanorods with thermoreversible, short-range attractions

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Colloidal suspensions containing anisotropic particles are widely utilized in consumer products, coatings, cements, food products, and pharmaceuticals. However, the effect of particle shape on the gel and glass transition boundaries is not well-understood for anisotropic particle suspensions, particularly for colloids with lower aspect ratios (AR, $L/D \sim 1-10$). The key aim of this study is to clarify the effects of particle shape and attraction strength on gel and glass transitions by exploring neutron scattering and other rheological methods. A new thermoreversible colloidal system has been developed, which is composed of hollow, octadecylcoated silica rods with dimensions of 30-200 nm, tunable aspect ratios, and short-range attractions. Following previously established water-in-oil emulsion methods^[1,2], silica rods are suspended in tetradecane, which enables thermoreversible gel transitions from fluid-like to solidlike states^[3]. Particles in nanoscale dimensions and hollow-core structure have shown to mitigate the effects of gravitational settling^[4] on the suspension fluid and gel microstructure. Thermodynamic and rheological behavior of such silica rods are characterized through a variety of powerful probing techniques. Particle size distributions are measured through dynamic light scattering and visualized through electron microscopy. Small amplitude oscillatory shear measurements confirm the thermoreversibility of the microstructure and its transition from fluidstate to gel-state. Lastly, small-angle neutron scattering methods provide critical information including the form factor of primary particles (shape, core and shell dimensions, brush conformation, size dispersity) as well as the interparticle attraction strength (T) and fractal dimension (D_f) of the fluid and gel microstructure. The results of this study will be of significant interest to a broad range of scientific disciplines in soft matter, molecular thermodynamics, and rheology, which share a common interest in the fundamental effects of particle shape anisotropy.

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Thermodynamics of ion-driven gelation of cellulose nanocrystal suspensions

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Ribbon-shaped cellulose nanocrystals (CNCs) are promising candidates as a building block for hydrogels because of their abundancy, renewability, potentially low production cost, and because of their interesting physical and chemical properties.^[1-4] They can also be prepared with ionic surface groups capable of interacting with dissolved ions to form ionotropically gelled materials. At high concentrations sulfated and carboxylated CNCs can also self-assemble to form a chiral nematic phase characterized by ordered left-handed helicoidal structures,^[5,6] with the ionic strength of the medium an important factor affecting chiral nematic phase formation.

Despite the interest in both the gelation and the chiral nematic structuring, little is known about the CNC-ion interactions.

We thus used isothermal titration calorimetry (ITC) to investigate the thermodynamics of interactions between cations of the second group of the periodic table and negatively charged cellulose nanocrystals (bearing carboxylate, sulphate, or a combination of both groups). The adsorption process was found to be endothermic and driven by an increase in entropy upon ion interaction. The effect was pH-dependent, showing an increase in enthalpy for cellulose suspensions at neutral pH (6.5) when compared to acidic pH (2). Surprisingly, interactions of CNCs bearing both sulphate and carboxylate groups were stronger with cationic ions than CNCs with a single functionality due to an increased entropy gain upon adsorption. Multiple functionalities thus increase surface structuring of water.

In addition, we found that the reduction in Gibbs free energy drives the ionotropic gelation of nanocellulose suspensions, and we show that ITC is able to detect gel formation at the same time as determining the critical association concentration.

I will present our findings and introduce ITC as a very valuable technique to study and gain more insight into ionotropic gelation of colloidal systems.

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Anisotropic viscoelastic phase separation in polydisperse hard rods: non-sticky gelation

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Background Spinodal demixing into two phases having very different viscosities leads to viscoelastic networks, i.e. gels.^[1] The demixing usually results from attractions between particles. **Aim** Here we consider demixing in a colloidal system of sterically stabilised clay rods, where one phase is a nematic liquid crystal with a strongly anisotropic viscosity. The polydispersity in particle aspect ratio results in a wide concentration gap between isotropic and nematic phases.^[2]

Methods We combine real space analysis of a sepiolite clay system with molecular dynamics computer simulations.

Results We find a long-lived network with many of the characteristics of a colloidal gel. Remarkably, the highly anisotropic viscosity means that flow is possible along the nematic director, but suppressed in other directions. The network structure is thus preserved, leading to a new form of gel. Our system presents a further novel property, in that it is comprised of hard particles.

Conclusion These dynamically anisotropic gels form in the absence of attraction between the particles. We show that our system exhibits the characteristics of gelation and conclude that it represents a new class of material, non-sticky gels in which attractions are not present.



Phase behaviour: nematic fraction on increase of volume fraction. (a) Confocal micrograph of nematic domains (scale bar 4 μ m) (b) Schematic of gelation of attractive particles.

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Formation of Gel Network in Fluorinated Material System

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Alpha-gel (α -gel) is one of attractive assemblies in the surfactant system and has been utilized for several applications because of its unique viscoelastic properties, emulsification, water retention, and so on. In general, a stable α -gel is formed by a mixture of surfactant and longchain alcohol at a given composition where these molecules can be arranged in the hexagonal sub-lattice. Thus, the α -gel is classified into solid state but macroscopically forms the threedimensionally interconnected network. On the other hand, the formation mechanism of α -gel has not been well understood yet and furthermore the studies on the α -gel formation have been reported in the hydrocarbon surfactant/hydrocarbon alcohol systems alone. Therefore, the motive of our study is to elucidate the phase behavior and α -gel formation of non-hydrocarbon materials. In addition, the physicochemical properties and structural information on this α -gel are discussed in comparison to the hydrocarbon homologues.

Sodium perfluorooctane sulfonate (RfSO₃Na) and 1H,1H,2H,2H-perfluoro-1-octanol (RfOH) were used as fluorinated surfactant and alcohol, respectively. The mixture of RfSO₃Na and RfOH at the mole ratio ([surfactant]/[alcohol]) =1/3 and the total amount of surfactant and alcohol in the system =10wt% formed the homogeneous, transparent gel-like solution in water at room

temperature (Figure 1), although any homogeneous solutions could not be obtained in each component/water binary system. The mixture of RfSO₃Na/RfOH/water was apparently liquid crystal, while the wide-angle X-ray scattering (WAXS) and calorimetry (DSC) measurements indicated the formation of α -gel. The lattice parameter of the hexagonal lattice was 0.51 nm for the fluorinated α -gel, which was incompatible with ~0.42 nm for the hydrocarbon one. This suggested that the lattice parameter is attributed to the packing of hydrophobic chain. In our presentation, we will show further unique optical and rheological properties of the α -gel composed of the fluorinated materials.

C16SO3Na/C16OH RfSO3Na/RfOH



Fig.1. Appearance of α -gels formed in C₁₆SO₃Na/C₁₆OH (left) and RfSO₃Na/RfOH (right). X_{S/A}=1/3, W_{SA}=10wt%.

Stabilization Mechanism of Quantum Dots by CTAB

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The cationic surfactant cetyltrimethylammonium bromide (CTAB) is widely used for preparation and stabilization of nobel metal quantum dots in aqueous dispersions. The specific role of CTAB-micelles in the formation process and the final stabilization is, however, still under discussion.

Here, a comprehensive analysis of extended small-angle X-ray and neutron scattering (SAXS/SANS) studies is presented which clearly demonstrates that the amount, size, and shape of the CTAB-micelles dominate the stabilization of small gold nanoparticles (seed-particles) in aqueous dispersion. These results are in perfect agreement with an analytical model based on particle collision statistics which will also be presented (cf. Fig. 1 and [1]).



Figure 1: Kinetics of gold-seed particle number evolution for seed particles stabilized with CTAB (black curve), CTAB/n-pentanole (red curve), and CTAB/n-hexanole (green curve) micelles. The influence of the orientation of the seed particle – micelle clusters (including the micelle anisotropy) on the gold-seed coalescence kinetics is illustrated in the left hand schematics.

The micelle concentration, size and shape could be analyzed in detail and finally controlled systematically by the total CTAB concentration, temperature, and concentration and type of additives, respectively. In particular, it has been found that the stabilization of gold seed-particles can significantly be enhanced when adding n-hexanol as an additive to the aqueous dispersion (cf. Fig. 1). The findings serve as a prerequisite to perform systematic studies on the formation of larger gold nanoparticles in a seed-mediated growth process.

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Controlling surface charge of pigment to enable reversible textile coloring

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Color removal is a bottleneck in textile recycling. Here, we present a coloring technology with an embedded decoloring function for pigment-dyed cotton fabric. Reversible adsorption of the hydrophobic pigment is achieved by stabilizing the pigment with a stimuli-responsive surfactant.

The stimuli-responsive surfactant is based on a branched amine that respond to CO_2/N_2 stimuli. The amine reacts with CO_2 to form a carbamate and reverts to its original form by exposure to heating and N_2 . In this study, N,N di(propylamino)dodecylamine (Y12-amine) an anionic carbamate-based surfactant (Y12-carbamate) was formed. First, we studied the surface activity of Y12-amine and Y12-carbamate by surface tension measurements using the pendant drop technique with a sealed chamber where the gas composition was controlled.

Second, the carbamate surfactant was used to stabilize the hydrophobic pigment. We show that the negative streaming potential of the pigment dispersed by Y12-amine in aqueous solution at pH 12, increased with time of CO_2 exposure because of the carbamate formation. Furthermore, the pigment was flocculated when the carbamate group was cleaved by exposure to N₂ and heating, and was re-dispersed by subsequent exposure to CO_2 .

Finally, we took advantage of this feature to reversibly color cotton fabric. The hydrophobic pigment, stabilized by the carbamate surfactant, was adsorbed on the surface of cationized cotton. Then, the carbamate was reverted to the amine by acid treatment, allowing the pigment to desorb that facilitates decolouring of the textile.

Surfactant Mediated Particle Aggregation in Nonpolar Solvent

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The importance of colloidal systems in many different processes, both natural and man-made, has led to a great development in this field in the last century. However most of these studies focused on aqueous systems, while surfactant-mediated colloidal dispersions in non-polar media received much less attention,^[1,2] while still being central processes in many different applications (*e.g.* electrophoretic displays, airborne drug delivery systems, and toner technologies).

This study aims at understanding the processes that governs colloidal dispersions in nonaqueous solvents: to this end aggregation of three different types of colloids in decane in the presence of AOT surfactant was investigated.

For these systems, which are only weakly charged in pure decane, charge reversal is observed with increasing surfactant addition, reaching a plateau at intermediate concentration range, before showing charge neutralization at the higher concentrations. This charging behavior, monitored by electrophoretic mobility measurements, is consistently mirrored by the stability ratios measured by DLS. It appears from this study that the colloidal dispersion behavior can be successfully explained by DLVO forces. Moreover, contrarily to what is normally observed for aqueous systems where screening of the double layer does play an important role in destabilization, in this case the aggregation behaviour is apparently driven by surface charging through adsorption/ desorption processes.



Figure 1: (a) Electrokinetic potential of silica in decane as a function of AOT concentration, (b) van der Waals interaction measured between two 4 μ m silica spheres measured in pure decane, (c) stability ratios of silica in decane as a function of AOT concentration.

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In-situ observation of agglomerating apolar nanoparticles in evaporating droplets by small angle X-ray scattering

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Colloidal stability is crucial for many applications of nanoparticles that include the inkjet printing of conductive structures, fabrication of optical nanocomposites, and quantum-dot enhanced sensors and displays. Several fabrication techniques involve the agglomeration or self-assembly of nanoparticles during solvent evaporation^[1] (i.e. out of stability), but little is known about this process. In general, the concentration-dependent agglomeration of apolar nanoparticles is not well investigated.

In our work, we aim to elucidate the agglomeration of nanoparticles in an evaporating solvent using time-resolved *in-situ* investigation of a "hanging droplet" (see figure 1). We use small angle X-ray scattering (SAXS) to simultaneously quantify nanoparticle agglomeration and solvent content. Particle agglomeration causes an increase in the structure factor; solvent evaporation is followed by measuring the "solvent peak" originating from the short-range order of the solvent molecules. Both features occur on different length-scales and are thus well-separated in the reciprocal space recorded by SAXS.



Figure 1: "Hanging droplet" experimental set-up to study *in-situ* nanoparticle agglomeration during solvent evaporation

We investigated gold nanoparticles stabilised by an octanethiol ligand shell dispersed in linear alkanes (heptane, nonane, decane), cyclohexane, and toluene. The concentration c' at which particle agglomeration sets in differed by almost two orders of magnitude from the worst (toluene) to the best (cyclohexane) solvent. We investigated whether there exists an equilibrium solution concentration c_s ("solubility") of non-agglomerated particles during the agglomeration process. We found such a solubility for all investigated solvents except cyclohexane; it was close to c' in all other cases. This finding indicates that concentration-dependent colloidal stability is similar to ideal molecular solubility in certain solvents, but not in cyclohexane. Other deviations from ideal solubility occur even in the alkanes, and we will provide first hypotheses on their origins.

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Properties of liposomes based on DPPC and β -sitosteryl sulfate

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Liposomes (Fig. 1) are spherical vesicles of phospholipid bilayers which are used in advanced drug delivery systems^[1]. Phosphatidylcholines (PC), a kind of phospholipids, are commonly used for preparing liposomes. An additive such as cholesterol is often used for achieving better elasticity, fluidity and stability in liposomes. However, an alternative to cholesterol for this purpose is necessary, not only for the associated health hazards but also for enhancing the efficiency of the drug carrier. In our earlier studies, β -sitosteryl sulfate (PSO₄) was found to interact favourably with the DPPC (dipalmitoylphosphatidylcholine) and DSPC (distearoylphosphatidylcholine)^[2] bilayers, which motivated us to investigate the properties of the corresponding liposomes.



Figure 1. Hydrodynamic diameter (D_H) as a function of storage period ^[2]. x = mole fraction of PSO₄

Figure 2. DPH fluorescence anisotropy (r_{dph}) as a function of mole fractions of PSO₄ (*x*)

For this study, 2 mM suspensions of the multilamellar vesicles (MLV) of DPPC, containing varying mole fractions of PSO₄ were prepared. Two portions of this suspension were sonicated with a bath sonicator and a probe sonicator, respectively, while the third portion was studied as such. Analysis of the samples was carried out with the help of spectrofluorometry, DLS (dynamic light scattering), and ζ -potential measurements. As shown in Fig. 1, the addition of even a small quantity of PSO₄ caused a significant decrease in the size of the multilamellar liposomes of DPPC. The liposomes containing up to 0.5 mole fraction (*x*) of PSO₄ are more stable against agglutination compared to the liposomes without it. Similarly, fluorescence anisotropy of the membranes decreases with increasing x indicating an increased membrane fluidity. The negative value of the ζ -potential increases significantly with the addition of PSO₄ ensuring a higher stability and dispersibility of the liposomes with enhanced efficiency, dispersibility and stability.

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Development of α-gel nanoemulsions using sodium methyl stearoyl taurate for stabilization of oil-soluble components

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Background: To develop a DDS carrier of oil-soluble active ingredients for cosmetics, reducing the size of the emulsion and increasing its skin permeability are important. Nanoemulsions containing a large amount of oil have been developed, including methods using a solubilization region [1] and phase inversion temperature (PIT) emulsification technology [2]. However, when applied as cosmetics, these emulsions have problems maintaining the stabilization of the oil-soluble components.

Aim: To overcome the problem caused by the weak interfacial strength of the emulsion, sodium methyl stearoyl taurate (SMT), an anionic surfactant, was examined as a potential new nanoemulsion. A combination of SMT and a fatty alcohol form α -gel in water [3]. New nanoemulsions with enhanced inclusion stability were developed by efficiently forming an α -gel on the interface of the emulsion using SMT and cetostearyl alcohol (CET).

Methods: By changing the molar ratio of CET and SMT formation of an α -gel was confirmed using differential scanning calorimetry (DSC). Nanoemulsions containing silicone oil were prepared using the α -gel, and the structure of the α -gel with various particle sizes was analyzed using DSC, wide angle X-ray diffraction (WAXD), and transmission electron microscopy (TEM).

Results: The DSC plots (Fig. 1) contained two different gel liquid crystal transition temperature peaks (CET/SMT=2.5 and 3.6). Based on the DSC, WAXD (Fig. 2), and TEM results, it was suggested that the higher temperature peak was assigned to the structure of liberated α -gel, and the lower temperature peak was assigned to the α -gel structure formed at the interface of the nanoemulsion.

Conclusion: A newly developed α -gel nanoemulsion could stabilize the oil-soluble component in water. Future studies will investigate its use as a lotion containing a large amount of oil and a carrier of DDS of various oil-soluble active ingredients.





Figure 1: Phase transition behaviour of SMT/CET/ methylpolysiloxane/water emulsion

Figure 2: WAXD profiles of SMT/CET/ methylpolysiloxane /water emulsion Diameter of (a) 80 nm, (b)110 nm (CET/SMT molar ratio=3.6)

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Encapsulation in double emulsions: Fabrication and time stability of the capsules

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Double water-in-oil-in-water emulsions are interesting systems for encapsulation of hydrophilic drugs (see Figure 1) as vitamin B12 or a suspension of Cydia pomonella Granulovirus, used in organic agriculture to protect fruits against the Carpocapse insect. Using rotor-stator mixers, monodisperse double emulsions were prepared in a two-step process that may impact the encapsulation efficiency. Using both classical UV-Vis spectroscopy and, more originally, rheology we assessed the encapsulation efficiency and water exchanges during emulsification ^[1]. We showed that encapsulation reached high levels, close to 100% and that this encapsulation decreased only if two conditions are fulfilled simultaneously: (i) during the second emulsification step the flow is turbulent and (ii) it leads to excessive fragmentation inducing formation of too small drops. We also discuss the effect of a deliberate osmotic pressure unbalance on the encapsulation and characterize the induced water fluxes.



Figure 1: Example a water-in-oil-in-water emulsion a) oil globule size distribution and b) microscopy image of the double emulsion: the inner droplets give the high contrast making the globule appearing dark.

Once prepared, these capsules could also release their content or exchange water between inner and external aqueous phases. Using the same techniques, rheology and UV-Vis spectroscopy, we built a lipophilic stabilizer concentration-inner droplet volume fraction diagram highlighting the domains where the double emulsion is stable towards encapsulation and/or water fluxes ^[2]. We showed the important role of non-adsorbed stabilizer concentration in the intermediate oil phase on the emulsion stability. In the non-stable domains, we describe the observed phenomena and we determine the mechanisms responsible for release.

We conclude that by a judicious choice of the composition, double emulsion may act as efficient capsules over a large period of storage.

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Stabilization of polyaniline-silica suspensions with polymers for anticorrosion applications

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Polyaniline (PANI) is a conducting polymer that can exist in different forms. Two forms of PANI are most extensively studied in anticorrosive coatings: the conducting emeraldine salt (ES) and non conducting emeraldine base (EB). The most extensively proposed mechanism of corrosion protection by PANI is the formation of a protective oxide layer at the metal/coating interface, induced by PANI as oxidizer. Despite the passivating effect, the coating consisting only of PANI cannot ensure complete metal protection. For that reason, a colloidal form of PANI can be used for obtaining of coatings of high adhesion to the metal surface and with good barrier protection. Preparation of particles-metal composite coatings with uniform properties necessitates retaining suspension's stability during incorporation of the particles into the metal coating.

In the present work, we describe the preparation of stable suspension of colloidal PANI-SiO₂ particles employing adsorption of commercially available triblock copolymer Pluronic F127 and cationic polyelectrolyte poly(ethyleneimine) (PEI). Steric stabilization of the suspension with positively charged particles (as ES) is realized at pH 3.5 by adsorption of Pluronic F127, while the adsorption of PEI onto negatively charged particles (as EB) provided electrosteric stabilization against aggregation at pH 5.5. Particles sizes and ζ -potential values are evaluated using electron microscopy, dynamic light scattering and electrophoresis. Stabilization of the PANI-SiO₂ suspension with polymers is followed for a period of 24 h. The polymer coated PANI-SiO₂ particles are then incorporated into the metal matrix of zinc in order to obtain composite zinc coatings on steel. The surface topography of the composite coating is investigated by SEM. The corrosion behavior of the coatings containing different forms of PANI (ES or EB) is evaluated with electrochemical measurements.

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Colloidal aggregation of magnetic nanoparticles with opposite-charge species in salty environment

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Colloidal stability of magnetic nanoparticles (MNPs) in salty environment is of the highest relevance in many biological or industrial systems. In the first case, the particles are internalized into cells, which are very complex media characterized by a high salinity and the presence of proteins and other species. The efficiency of the MNPs for the proposed biological applications is directly linked to their aggregation state in the cells. In the second case, nanoparticles dispersed in pure ionic liquids, which can be seen as extreme salty systems, have potential applications in heterogeneous catalysis, heat-transfer fluids and they can be used as gels for dye-sensitized solar cells and gas sensors.^[1]

As a model system, we studied the colloidal stability of a medium composed of maghemite nanoparticles negatively charged by the adsorption of polyacrylate ^[2], of added ions with different concentrations and of a polycation, ionene ^[3], with various charge densities. We can thus follow the evolution of the electrostatic interaction between oppositely charged species (negative NPs and polycation) in a salty environment going from aqueous salt-free solution, where the electrostatic interaction is supposed to dominate, to almost pure ionic liquid ^[4], where a new long-range force was recently evidenced ^[5].

We varied the nature of the added salt using substituted ammonium salts and its concentration between 0 mol/L up to 11 mol/L in the case of ethylammonium nitrate. It was concluded, that

- colloidal stability is obtained at *high* salt concentration, which is absolutely uncommon
- the concentration threshold for aggregation depends on the nature of the added salt, indicating that simple electrostatics is not sufficient to understand these systems.

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Many-body depletion interactions between particles in a polymerizing system

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We have recently developed an analytical theory for the many-body potential of mean force (PMF) between *N* spherical particles immersed in a polymer solution. The analytical expression for the PMF allows for computer simulations where the *complete N*-body potential is employed. A crucial aspect is that the many-body PMF that is utilized in the simulations only *requires summations over particle pairs*. Hence, these simulations are no more demanding than if they interact via a standard pair potential. The computational saving compared to an explicit polymer model, can of course be enormous. An evaluation of many-body theory is given in Figure 1, where data from explicit and implicit polymer simulations are compared.

Particles (R_S) + non-adsorbing polymers $(R_G = 2R_S)$ solid: explicit polymers; dashed: many-body potential



Figure 1. Particle-particle radial distribution functions (g(r)), in colloid-polymer mixtures, under non-adsorbing conditions. The polymers are twice as large as the particles, whereby many-body interactions are important. As the particle volume fraction increases, depletion interactions lead to a phase separation, as manifested by a long-ranged slope in g(r). The explicit polymer simulations (solid) are computationally demanding (more than 10^6 monomers), whereas a many-body simulation (dashed) is finished within a minute on a laptop.

According to semi-grand simulations, as well as mean-field theory, where the many-body potential is used, many-body interactions have a *profound* effect on the particle phase diagram, leading to exceedingly dilute coexisting particle phases, as the average polymer length increases, under the constraint of a constant monomer density. The latter constraint is commensurate with a polymerizing system.



Figure 2. Phase diagrams, for a system containing a Θ solvent, at constant monomer concentration. The particle volume fraction is denoted by η . Notice how a pair approximation will lead to the prediction of a monotonically *increasing* demixing region, in qualitative disagreement with a many-body treatment.

Unfortunately, a verification of these predicted phase behaviours, by comparisons with explicit polymer simulations, would require an insurmountable computational effort. However, we have quite recently been able to verify that the phase behavior of thin polymerizing rod-like particles + spherical particles is qualitatively in agreement with the many-body prediction for flexible chains + particles. Explicit rods+particles can be simulated at a reduced computational expense. These rod+particle simulations also highlight the fact that even though the impact of depletion on the particle-particle g(r) is quite modest in the long rod limit, a phase transition will occur already at very low particle concentrations.

Many-body interactions causes the coexistence region to close up and form a cusp for very long polymers. This is in stark contrast to the often used pair approximation, where only 2-body forces are considered to act, as illustrated in Figure 2.

Temperature sensing in cells by polymeric upconversion nanocapsules

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Monitoring local temperature in cells is essential to understand their biological activities since the enhanced cellular metabolism leads to higher heat production which can be a sign of diseases like cancer.^[1] One technological barrier is that the temperature probe must be biocompatible and small enough to be incorporated in the cellular environment without disturbing the cell metabolism. Polymeric nanocapsules^[2] offer a solution to overcome such challenges due to their flexible structure design. Therefore, herein, we report polymer-based upconversion nanocapsules^[3] for potential use as nanothermometers in cells. The nanocapsules utilized the temperature dependence of a special optical phenomenon called 'triplet-triplet annihilation upconversion (TTA-UC)' that enables the conversion of low energy photons (λ_{exc} = 633 nm) into high energy ones (λ_{em} = 520 nm). The miniemulsion solvent evaporation method was applied to synthesize the nanocapsules comprised of a PMMA shell and a core of rice bran oil containing the TTA-UC active dyes. The sensitivity of the TTA-UC on the local oxygen concentration was overcome by the oxygen reduction ability of the rice bran oil core to trigger this event, even in ambient environment. By this, calibration curves, connecting the local temperature (22 °C up to 40 °C) and the emission parameters of the TTA-UC signals, were obtained when nanocapsules were taken up by HeLa cells. Thus, the temperatures approaching to the enhanced metabolic activity range of the HeLa cells led to a significant rise in the delayed fluorescence spectrum of the nanocapsules. This opens up new opportunities for developing novel treatment and diagnostic tools in medicine.



Figure 1: Polymeric upconversion nanocapsules (UCNCs) sensing the temperature in HeLa cells – Cellular uptake and core/shell structure of the UCNCs are shown in the CLSM image and in the TEM micrograph, respectively.

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Directed-assembly of Colloidal Shuttles and Micromachines for Programmable Cargo Delivery

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External field gradients are commonly used for separation, contactless manipulation^[1] and assembly^[2] of nano- and microparticles. Here, we introduce a novel colloidal shuttle by using electric field gradients, so called dielectrophoresis. In a homogenous electric field, a dielectric colloid can act as a field gradient-maker and change the electric field strength around itself. Such field strength alteration around the dielectric colloid was employed as a trap for other particles. Orthogonally using magnetic fields in addition to electric fields and employing magnetic "shuttle-colloid" allowed for loading, transporting and unloading of the trapped cargo. This technique was extended to transport bio-cargo and anisotropic colloids ^[3]. Furthermore, such interactions can be used to reversibly program and assemble microrobots and mobile micromachines ^[4].



Figure 1: A novel active transport system for colloidal cargo transportation with electric field load-unload function where magnetic field gradient serves for motion of the cargo and the carrier.

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Overcoming antibacterial resistance by surface functionalised and self-grafting antimicrobial nanocarriers

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Multidrug-resistant pathogens are prevalent in chronic wounds. There is an urgent need to develop novel antimicrobials and formulation strategies that can overcome antibiotic resistance, and provide a safe alternative to traditional antibiotics. We developed a novel functionalised polyacrylic copolymer nanogel carrier for two cationic antibiotics, tetracycline and lincomycin hydrochloride, which can potentially overcome antibiotic resistance.^[1] These antibiotic-loadd nanogels were further surface functionalised with a biocompatible cationic polyelectrolyte, bPEI, to increase their affinity towards the negatively charged bacterial cell walls. We assessed their action against a range of wound isolated pathogens, which had been shown through antimicrobial susceptibility testing (AST) to be resistant to tetracycline and lincomycin. Our data reveal that bPEI-coated nanogels with encapsulated tetracycline or lincomycin displayed increased antimicrobial performance against selected wound-derived bacteria, including strains highly resistant to the free antibiotic in solution (Fig.1A). Our nanocarrier-based antibiotics showed no detectable cytotoxic effect against human keratinocytes. This approach may breathe new life into a range of existing antibiotics, offering a new mechanism to overcome antibiotic resistance.^[2,3]

In addition, we developed and tested a novel formulation of copper oxide (CuONPs) functionalized with (3-Glycidyloxypropyl)trimethoxysilane (GLYMO) to allow further covalent coupling of 4-hydroxyphenylboronic acid (4-HPBA). As the boronic acid (BA) groups on the surface of CuONPs/GLYMO/4-HPBA can form reversible covalent bonds with the diols groups of glycoproteins on the bacterial cell surface, they can strongly bind to the cells walls resulting in a very strong enhancement of their antibacterial action which is not based on electrostatic adhesion.^[4] We demonstrate that the CuONPs with BA-surface functionality are far superior antibacterial agents compared to bare CuONPs. Our results showed that, the antibacterial impact of the 4-HPBA functionalized CuONPs on *E.coli* and *R. rhodochrous* is one order of magnitude higher than that of bare CuONPs or CuONPs/GLYMO. We envisage that formulations of CuONPs/GLYMO/4-HPBA can be used to drastically reduce the overall CuO concentration in antimicrobial formulations while strongly increasing their efficiency.



Figure 1: A: Schematics of the antibiotic loaded nanogel particles. Minimal inhibitory concentration (MIC) for free and nanocarrier-based tetracycline against susceptible and resistant bacterial strains. (B) The interaction between the CuONPs/GLYMO/4-HPBA and the sugar groups on the surface of the bacterial cell wall leads to their attachment to the bacterial cell wall which strongly amplifies their antibacterial action.

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Nonequilibrium uptake kinetics of molecular cargo into hollow hydrogels tuned by electrosteric interactions

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Hollow hydrogels represent excellent nanocarriers due to their ability to encapsulate and release large amounts of cargo molecules (cosolutes) such as drugs or proteins. We use a combination of an effective cosolute-hydrogel interaction potential and dynamic density functional theory to investigate the nonequilibrium encapsulation kinetics of charged and dipolar cosolutes by an isolated charged hollow hydrogel immersed in a 1:1 electrolyte aqueous solution. Our analysis covers a broad spectrum of cosolute valences (z_c) and electric dipole moments (μ_c), as well as hydrogel swelling states and hydrogel charge densities. Close to the collapsed state, the encapsulation process is hindered by the excluded-volume interaction exerted by the polymer network. Different kinetic sorption regimes are found depending on the values of z_c and μ_c . For cosolutes of the same sign of charge as the gel, the superposition of steric and electrostatic repulsion leads to an *interaction-controlled* encapsulation process, in which the characteristic time to fill the empty core of the hydrogel grows exponentially with z_c . On the other hand, for cosolutes oppositely charged to the gel, we find a *diffusion-controlled* kinetic regime, where they tend to rapidly absorb into the hydrogel membrane and the encapsulation rate depends only on the cosolute diffusivity. Finally, for large μ_c , the kinetics enters an adsorption-hindered diffusion, where the enhanced surface adsorption imposes a barrier that slows down the uptake. Our study represents the first attempt to systematically describe how the swelling state of the hydrogel and other leading physical parameters determine the encapsulation process^[1].



Figure 1: Schematic Illustration of cargo uptake into a hollow hydrogel

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Tunable biocompatible catanionic vesicles from amino acid-based surfactants: from rational design to drug delivery

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Vesicles assembled from suitable blends of cationic and anionic surfactants offer several distinctive features compared to conventional liposomes, namely facile formation, long-term colloidal stability, chemical robustness and versatility of size, surface charge and gel-to-liquid crystal phase transition temperature (T_m). For nanomedical applications, biocompatibility, biodegradability and low toxicity are further pivotal. In this realm, amino acid-based surfactants are deemed as good candidates to target the design of robust, physiologically relevant vesicles. In our group, we have developed in recent years a number of novel cationic and anionic amphiphiles of assorted molecular structure based on amino acid motifs, in particular serine.^[1,2] Herein, we will first report on studies encompassing detailed phase behavior maps looking for regions of net cationic and net anionic vesicles, followed by the structural characterization of the aggregates in terms of size, pH and zeta potential.^[3] Recently, the *in vitro* performance of some selected catanionic fully serine-based vesicles (Figure 1) has been investigated using a cancer cell model for the delivery of the anti-cancer drug doxorubicin (DOX).^[4]



Figure 1: Fully serine-based catanionic vesicles as efficient nanocarriers for anti-cancer DOX.

DOX is successfully encapsulated in the vesicles, resulting in surface charge switches that are relevant for systemic administration. High cell uptakes are demonstrated, with drug accumulation resulting in up to 2.5-fold increase compared to free DOX and with localizations near the nuclear regions of the cells. The *in vitro* cytotoxicity studies show that DOX-loaded vesicles induce cell death, confirming the therapeutic potential of the formulations. Furthermore, the efficient accumulation of the drug inside the cell compartments harbors the potential for optimization strategies.

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Hybridosomes®: Innovative Multifunctional Nanocapsules from the Ouzo Effect

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We report on a new method to generate hollow capsules with a hybrid shell made of nanoparticles and polymers, which were coined "Hybridosomes".1 The process is based on the formation of droplets in macroscopically miscible mixtures of water and an organic solvent containing a hydrophobic solute and nanoparticles, the so-called "ouzo effect". Our hypothesis is that nanoparticles stabilize such submicronic droplets by adsorbing at the liquid/liquid interface, similarly to Pickering emulsions. After addition of a crosslinking polymer and removal of the solvent core, hollow and porous capsules of diameter ~100 nm are obtained. They have been widely characterized in liquid and dried state in term of structure, size tunability, shape, surface properties with routines techniques (TEM, SEM, DLS, Nanoparticle Tracking Analysis, UV-vis). For instance, these versatile nanocapsules can be prepared from iron oxide nanoparticles (IONP), gold nanoparticles (AuNP), Quantum Dots (QD) and their mixtures. As a nanocarrier we also demonstrated their ability to encapsulate an organic dye. The soft shell of Hybridosomes® was investigated for a single object by AFM nanoindentation and at the ensemble level using an osmotic compression technique.² It was found that the Hybridosomes® exhibits a soft and deformable shell with a Young's modulus of 1MPa, which explains their outstanding mechanical properties, such as long term stability, easy deformation and shape recovery. Interestingly, the magnetic/fluorescent nanocapsules enable Magnetic Resonance Imaging contrast enhancement of tumors in vivo¹ and fluorescence imaging. Hybridosomes® therefore present a real potential for biomedical applications such as imaging and/or drug encapsulation, delivery and release.³



Figure 1: A: Schematic representation of Hybridosomes®, B: TEM micrograph of mixed IONP/AuNP@PAA Hybridosomes® and C: magnetic resonance image of mouse liver 30min after injection of IONP@PAA Hybridosomes®

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Design of peptide targeted nanovesicles for the α -galactosidase A enzyme delivery

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Fabry Disease is a rare lysosomal storage disorder characterized by a lack of a metabolic enzyme, α -galactosidase A (GLA), leading to an accumulation of glycosphingolipids in cells. Enzyme replacement therapy, in which recombinant GLA is administered intravenously to patients, shows some drawbacks related to the poor biodistribution, limited efficacy and relatively high immunogenicity.

An attractive strategy to improve GLA efficacy is its encapsulation in nanocarriers ^[1]. We have studied the GLA encapsulation in targeted nanoliposomes functionalized with RGD-peptide to provide shell protection and specific delivery to target cells ^[2]. Nonetheless, this GLA-nanoliposomal system still needs optimization to overcome issues such as poor colloidal stability and low drug loading capacity. In this work we explore the use of two different RGD-targeted nanovesicles for GLA entrapment: Quatsomes ^[3-4] and Hybrid-Liposomes, both containing the quaternary ammonium surfactant Miristalkonium chloride (MKC) in high and low amount, respectively. Formulations were prepared using one-stage procedure based on compressed CO₂ ^[5]. Physicochemical parameters, GLA loading and enzymatic activity were characterized to select the best prototype. *In-vitro* and *in-vivo* safety was also evaluated.

It was seen that positive surface charge provided by the cationic surfactant MKC promotes the electrostatic interaction between the enzyme (isoelectric point: 5.1) and the nanovesicle, increasing their loading capacity. Additionally, the electrostatic repulsion between vesicles equally charged improves the colloidal stability preventing aggregation. However, the use of high quantities of MKC as in the case of Quatsomes provokes a considerable reduction in GLA enzymatic activity; this is not the same for Hybrid-Liposomes, where enzymatic activity is maintained and even higher than the non-encapsulated GLA.

Improvement of critical quality attributes such as increased colloidal stability and large entrapment efficiency allows the reduction of the injected volume of nanoformulation necessary to achieve efficient GLA levels, an extremely important issue to fulfil the requirements for preclinical assays.

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Encapsulation of novel conjugated polymers in biocompatible microemulsions: Application in theranostics

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The development of "soft" nanoformulations, as carriers of compounds with biomedical interest, is a technology with applications ranging in various fields. In particular, the use of microemulsions enables the enhanced, controlled and targeted delivery of bioactive compounds, while increasing their solubility and bioavailability. Recently, conjugated polymers have attracted attention in biomedical field, from sensors to *in vivo* imaging techniques and cancer therapy. Due to the polymers' strongly lipophilic nature their delivery still remains a major issue.

In the present study, biocompatible, oil-in-water microemulsions composed of water, sorbitan monooleate, Labrasol® and limonene were developed to encapsulate and deliver novel near infrared (NIR) absorbing conjugated polymers namely PBDT-DPP and PIDT-TDQ. PBDT-DPP comprises of benzodithiophene and dithienyl diketopyrrolopyrrole (DPP), whereas the PIDT-TDQ consists of indacenodithiophene (IDT) and thiadiazoloquinoxaline (TDQ). PBDT-DPP is a NIR-I absorbing polymer with an optical bandgap (E_g^{opt}) of 1.44 eV and PIDT-TDQ is a NIR-II absorbing polymer with an E_g^{opt} of 1.05 eV [1].

Structural characterization of the system in the absence or presence of in-house synthesized polymers was performed by means of Dynamic Light Scattering (DLS) and Electron Paramagnetic Resonance Spectroscopy (EPR). DLS provided information about the diameter and size distribution of oil nanodroplets upon encapsulation of the compounds and upon different storage temperatures. Interfacial properties of microemulsions were investigated performing EPR spectroscopy and spin probes of different polarity, namely 5-doxyl stearic acid (5-DSA), 16-doxyl stearic acid (16-DSA) and 10-doxyl nonadecane (10-DN) were used [2].

Regarding the biological evaluation, inhibition of cell proliferation in various cancer cell lines was tested through the MTT assay. Empty and loaded microemulsions were administrated in a range of concentrations for 48h, 72h after the treatment onset. Neither nanocarrier nor encapsulated polymers exhibited significant cytotoxicity. Confocal Laser Scanning Microscopy (CLSM) was used for testing the intracellular release of the encapsulated polymers.



Figure. PIDT-TDQ and PBDT-DPP loaded microemulsions.

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Encapsulation stability and pH-dependent release kinetics of phytopharmaceuticals from polysaccharide-based microparticles

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Over the past decade, there has been increasing interest in the use of plant-derived products in enteral formulations targeted to phytotherapies. Of importance are encapsulation approaches leading to microcarriers that can deliver drugs to target places with higher efficiency and reduced systemic toxicity. The sustained, controlled or "on-demand" release abilities are among the key features of drug microcarriers. The rate and mechanism of the release relies on various physicochemical properties of the carrier, i.e. particle size, composition of the core, presence of the outer layer, type and properties of the layer, etc.^[1-3] Hence, we have studied two kinds of hydrogel microparticles fabricated using ionotropic gelation by means of emulsification and extrusion methods. Various combinations of alginate or carboxymethylcellulose were applied as the core materials, and chitosan or gelatin - as the coating building blocks. The studied microhydrogels were loaded with a natural model drug (i.e., esculin, hesperidin, *Thymus vulgaris* essential oil). The following features were studied: effect of morphology, composition and structure of the microcarriers on kinetics and mechanism of the payload release under gastric conditions in vitro. It has been shown that a defined quantity of payload can be repeatedly released from polysaccharide-based microparticles "on-demand" by pH values and activity of digestive enzymes in the gastrointestinal tract. This makes the fabricated microcarriers potential candidates for applications such as controlled drug delivery or study of reaction-diffusion phenomena in simulated physiological conditions. The microparticles provided not only various pathways to the diffusing molecules, but also sustained release over a long time (up to 48 h). The fast release kinetics was predicted by a first-order or Korsmeyer-Peppas models, while the slow release kinetics was predicted by Higuchi or Gallagher-Corrigan models. Our findings demonstrate that the investigated polyelectrolyte-based microparticles provide a practical approach for sustained drug delivery for oral therapy.

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Mucin hydrogel embedding nanoparticles for transmucosal delivery.

Structure and dynamics by SANS, SAXS and XPCS.

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Mucins are the major components of the mucosal barrier covering several body tissues. The mechanical and rheological properties of mucus mainly depend on the structure and dynamics of the mucin hydrogel that originate from the competing hydrophilic and hydrophobic nature of adjacent domains along the peptide backbone. In fact, about the 80% of the total mucin molecular weight is accounted for by sugar chain branches, extending from the backbone and building up the hydrophilic domains. Indeed, the interplay between structure and dynamics confers to mucus gel its biological functions and a defective mucus flow is at the base of some of the most critical pulmonary pathologies, such as Cystic Fibrosis (CF). To improve the understanding of the nanoscale structure of the mucin hydrogel we exploited the contrast matching opportunity offered by neutron spectroscopy in complementary neutron and X-ray small angle scattering (SANS and SAXS) studies. We distinguished contributions of the sugar network and of the overall backbone mesh to the scattering profile. We extended the study to mucus models enriched in DNA applied in mucus/nanoparticles (NPs) interaction investigation, preliminary to vector design for lung treatment in CF. We probed mucin mesh dynamics by high-energies X-ray Photon Correlation Spectroscopy (XPCS) applying both silica particles and actual NPs designed for siRNA delivery, as tracers. NPs were size tuned to the length scale relevant to the topological entanglements of mucin and mucin/DNA meshes, in order to provide information on the fluctuations of the mesh within their local environment. Correlation functions highlighted the presence of a very slow dynamics. An unexpected q-dependence of the correlation function relaxation times was also observed. XPCS can provide valuable information on the delicate dynamic regulation of mucus swelling and rheology.

WouHa, hydrogels for increased wound healing rate

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Chronic wounds, such as venous leg ulcers, diabetic foot ulcers, and pressure ulcers, are common health problems in the elderly and the obese. Treatment options are limited and are mostly based on the use of wound dressings and/or hydrogels. Chronic wounds can cause severe morbidity and create a grave burden on the patients and their environment. Because of the limited understanding in the underlying pathophysiological processes of wound healing, it remains challenging to identify potential treatment options that have a positive effect on wound healing. We have developed a hydrogel formulation based on the gelation of glycyrrhizin in water. This compound also acts as an active component that directly inhibits a protein recently identified by us and our collaborators at the Vlaams Instituut voor Biotechnologie (VIB) as a key element of an important pathway in wound healing inhibition and, more specifically, in diabetic wound healing inhibition. We thus developed **fully degradable physical hydrogels that can be used as wound dressing where the gelation agent also has active anti-inflammatory properties** that enable faster wound healing.

Due to the biomedical application, a proper rheological screening is needed to optimize their application range on human wounds. A standard rheological screening is applied on hydrogels with a concentration range between 2.5-10 m%. The remarkable gelation behavior is caused by fibril formation, this was only demonstrated in lower hydrogel concentrations ~2 m%. To fully acknowledge the structure formation a temperature and concentration dependent Small Angle X-ray Scattering was also applied (SAXS) and will be presented.

A major part of this task was the optimization of the applied geometry as the hydrogels have a large difference in strength depending on temperature (1 Pa up to 10⁶ Pa for G' and G"). Next to this, these hydrogels were successfully applied on mice and pigs to correlate rheology with the biomedical applications.

Structural characterization of Nanoparticles for drug delivery: tuning nanostructure and mucus interaction

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Nanoparticles and nanoemulsions composed by a hydrophobic core stabilized by physiological lipids or surfactants have been widely proposed as efficient vectors for mucosal drug delivery. Besides optimal encapsulation, the design of the best vectors has to face key properties as tissue targeting and drug controlled release. According to the final target, the selected administration route and the delivery strategy, mucoadhesive or mucopenetrating agents, like chitosan and PEGylated surfactants, profitably modulate the residence time and the interaction of nanoparticles with the mucus barrier. We applied a complete structural characterization of different new nanovectors designed by non-conventional association of chitosan for ophthalmic and nasal administration. On the whole particle length-scale, the particles size and morphology and the surface charge were assessed by Dynamic Light Scattering, Atomic Force Microscopy and Zeta Potential respectively. The shape and the internal structure of the nanoparticles were studied by Small-Angle X-ray and Neutron Scattering (SAXS and SANS). When useful, Wide-Angle X-ray Scattering was applied to get details on the very local structure (Angstrom lenghtscale). Also Differential Scanning Calorimetry was employed to get hints on the interference and intraparticle distribution of admixed compounds. Combined results guided the realization of chitosan-associated formulations with the optimal structural properties and allowed for determining their propensity to interact with the mucin gel and their biodegradability by enzymes typical of the mucus layer, such as lysozyme. Notably, the presence of chitosan, as a simple adjuvant in the solution, showed up to have a positive impact on the diffusion of PEGylated nanoparticles through the mucin matrix, enlarging its mesh size. Then, coupling mucoadhesive and mucopenetrating agents reveals as a promising strategy for innovative transmucosal delivery systems. The accessibility of structural properties on different lenghtscales and with enhanced selective visibility comes out to be fully functional to the description of complex interacting colloidal biosystems.

MED3-1

Colloids in Medicine & Controlled Release Effect of Endogenous Molecules on the Interfacial Properties of Silicone Oil for **Ophthalmic Surgery**

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Background: Silicone Oils (SOs) are used in ophthalmic surgery as substitutes of the vitreous humour, the gel filling the vitreous cavity. However, SOs tend to emulsify with the aqueous phase produced in the ocular cavity, possibly causing severe post-surgical complications. Recent studies have suggested a role in the emulsification of surface-active endogenous biomolecules ^[1], which are present in-situ due to post-surgical inflammatory state. Systematic studies concerning the effects of blood proteins on the key chemico-physical properties of the SO-aqueous interface are not available ^[2].

Aim: This work aims at understanding the chemico-physical properties of SOs-aqueous solutions interfaces in presence of surfactant biomolecules, for the development of new strategies to reduce the emulsification process after surgery.

Methods: We have investigated the effects on the interfacial tension and the dilational rheology of solutions of selected blood proteins (bovine serum albumin and bovine y-globulins) at various concentrations, simulating the in-vivo protein environment. A similar study was carried out on the effects of solutions of whole human blood serum (WHBS). Measurements were performed using a Drop Shape tensiometer (PAT-1, Sinterface), properly set up to deal with the high viscosity of SOs and of the small difference between its density and those of the investigated aqueous solutions.

Results: A significant decrease of interfacial tension was observed for physiologically realistic protein concentrations even if slight compared with that of common surfactants. The effects on the dilational rheology are important, especially for WHBS, which shows an elasticity of the order of 100 mN/m already at low concentrations.

Conclusions: The results call for a picture where, even if emulsification is only slightly facilitated by the presence of biomolecules, the generated emulsions significantly stable against coalescence. Further studies are under way to validate these conclusions by investigating the SO emulsification in a model of the eye cavity.

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Wrapping or trapping? Halloysite and negatively-charged polyelectrolytes interactions

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Halloysite Nanoclays (HN) are attracting an ever growing interest as biocompatible versatile nanocarriers due to the possibility to load compounds into their lumen or on their external surface. Several investigations show that a large variety of active agents and charged biopolymers can be efficiently loaded/adsorbed and used for a range of applications. Only few attempts were proposed for the adsorption/loading of nucleic acids, such as DNA,^[1] antisense oligodeoxynucleotides^[2] and siRNA^[3]. It is generally ascertained that negatively-charged biopolymers enter the lumen through a combined effect of capillary action and electrostatic attraction, while DNA is proposed to wrap around HNs.^[1] As nucleic acids are negatively charged polyelectrolytes, this finding is somewhat surprising. Due to the high potential of HNs as nucleic acids nanocarriers, systematic investigations on the interaction of HN and nucleic acids are, therefore, in urgent need. In this study, we propose to investigate the interaction between negatively-charged polyelectrolytes (calf thymus DNA, and Sodium Polyacrilate, NaPA) and HN nanoclays by an experimental approach based on Dynamic Light Scattering, electrophoresis, Electron and Atomic Force microscopy and spectroscopic techniques. NaPA a linear flexible polyelectrolyte, has been chosen as model polyanion for DNA. Different lengths were tested to assess stiffness and molecular weight effects. Our results give evidence that the interaction with negative polyelectrolytes significantly improves the stability of the dispersion of the HN suspensions, in a concentration-dependent manner. For NaPa, no intimate interactions are present and no difference is observed at increasing chain length. The stabilization of the HN/NaPA complexes is mainly connected with effect of pH changes due to polyelectrolyte hydrolysis. On the contrary, in the case of DNA, a significant interaction has found with different details dependent on the different single-or double-stranded DNA conformation.



Figure 1: adsorption isotherm of denatured (red) and native (blue) DNA on HN at 25 °C. In the inset, examples of raw and covered HN obtained by SEM.

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The fate of therapeutic nanoparticles in a model biological medium: interactions with serum albumin

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In the field of nanomedicine, nanostructured nanoparticles (NPs) made of self-assembling prodrugs emerged in the recent years. In particular, the squalenoylation concept has been applied to several therapeutic agents with promising results.^{1,2} These nanoparticles allow a high encapsulation rate of the active principle, the protection from quick degradation, and a good control of the targeting and release. Beyond the high potential of these Nps, there is still a need for a better understanding of their evolution in biological media. The colloidal stability of the NPs, their interaction with proteins and how the internal NPs nanostructure influences their efficacy are essential questions to go towards a better understanding of the mechanism of their fate in the organism (nanoparticle disassembly, targeting etc...).

We choose to investigate these questions on the particular case of Squalene-Adenosine (SqAd) nanoparticles,³ whose neuroprotective effect has already been demonstrated in murine models and model biological media⁴. From the combination of multiple techniques (neutron and x-ray scattering, cryogenic transmission electron microscopy, circular dichroism, fluorescence spectroscopy, isothermal titration calorimetry and DFT calculations) we investigate the interactions between the SqAd Nps and the serum albumin, one of the main proteic components of blood plasma. We show that albumin affects the colloidal stability of the nanoparticles but also partially disassembles the nanoparticles by forming SqAd-albumin complexes. Albumin should thus play a crucial role in the transport of the prodrug, while the nanoparticles would act as a circulating reservoir in the blood stream.⁵

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Lamellar and Curved Model Membranes Probing the Interaction at the Nano-Bio Interface

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One of the most compelling goals of Nanomedicine is to achieve a physicochemical understanding of Nano-Bio Interfaces, as ideal platforms probing the interaction between engineered nanomaterials and biological barriers, like plasma membranes of cells. Notwithstanding the technological advancement in the design of smart nanomaterials for biomedical applications, their clinical translation has been limited to date, mostly due to the lack of grounded predictive models, describing their behavior in biological fluids and cytotoxicity. In this framework, lipid-based biomimetic systems are essential tools to mimic biological interfaces under simplified conditions ^[1], allowing for the identification of key determinants implied in the biological fate of nano-sized materials. Here, inorganic nanoparticles endowed with diverse physicochemical nature have been challenged with 2D lamellar model membranes of varying composition and fluidity, as well as with 3D non-lamellar biomimetic mesophases ^{[2] [3]}, mimicking curved membranes of diseased cells. Combining optical (UV-Vis Spectroscopy and Confocal Laser Scanning Microscopy), structural (Small-Angle Neutron and X-Ray Scattering) and surface (X-Ray Reflectivity, Quartz-Crystal Microbalance and Liquid Atomic Force Microscopy) techniques, we provide new perspectives on the mechanism underlying the interaction of nanoparticles with biological interfaces, where the molecular origin of colloidal self-assembly is disclosed [4]

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pH-Switchable Nanocarriers for Targeted Delivery of Antimicrobial Peptides

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In light of the global surge of antibiotic resistance, membrane active antimicrobial peptides are a promising alternative to conventional antibiotics.^[1] Stimuli-responsive nanoparticles based on the colloidal self-assemblies of surfactant-like lipids have the potential to provide targeted delivery of AMPs, reducing their side effects while protecting them from degradation in physiological environments.^[2,3]

Here, the design and characterization of pH-responsive antimicrobial self-assemblies of oleic acid (OA) and human cathelicidin LL-37 are presented.^[2] The colloidal structure of the binary LL-37/OA self-assemblies was characterised, depending on the composition and pH-values, using synchrotron small angle X-ray scattering (SAXS), cryogenic transmission electron microscopy (cryo-TEM), and dynamic light scattering. Nanostructural transformations from negatively charged core-shell cylindrical micelles with a cross-sectional diameter of 5.5 nm at pH 7.0 to positively charged aggregates of branched threadlike micelles at pH 5.0 were detected. *In vitro* antimicrobial assays using an *Escherichia coli* bacteria strain showed high bactericidal activity of the LL-37/OA aggregates at pH 5.0, but negligible activity of their cylindrical micelles at pH 7.0. The nanocarriers' ability to reversibly switch between its biologically active and inactive state upon changes in pH could be used to passively target the activity of antimicrobial peptides to locations of specific pH in the body. The presented findings improve our fundamental understanding of the interactions during peptide-lipid self-assembly and pave the way for further design of simple pH-responsive delivery systems for antimicrobial peptides.



Figure 1: pH-switchable bactericidal activity of the LL-37/OA nanocarriers (red curves) and LL-37 alone in solution (blue curves) against *E.coli* at pH 5 and 7. The nanocarriers showed high antimicrobial activity at pH 5.0, comparable to that of LL-37 alone, but showed no activity at pH 7.0. Adapted from [2].

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Hot-spot effect for remotely triggered drug delivery from magnetic nanocarriers

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Magnetic hyperthermia which exploits the heat generated by magnetic nanoparticles (MNP) when exposed to an alternative magnetic field (AMF) is now in clinical trials for the treatment of cancers. However, this thermal therapy requires a high amount of MNP in the tumor to be efficient. On the contrary the hot spot local effect refers to the use of specific temperature profile at the vicinity of nanoparticles for heating with minor to no long-range effect. This magneto-thermal effect can be exploited as a relevant external stimulus to temporally and spatially trigger drug release. ^[1]

We will highlight recent studies illustrating the use of the hot-spot effect for drug delivery in two examples: magnetic nanogels and magnetic molecularly imprinted polymer nanoparticles.

In one hand, biocompatible and thermo-responsive nanogels were prepared by conventional precipitation radical co-polymerization in water and post-assembled by complexation with MNP. These magnetic nanogels have a swelling-deswelling behavior at their volume phase temperature transition (VPTT) around 47 °C in a physiological medium (pH 7.5) (Figure 1a). In cancer cells, not only the magnetic nanogels internalize doxorubicin (DOX) more efficiently than free DOX, but also DOX intracellular release can be remotely triggered under AMF, in athermal conditions, thus enhancing DOX cytotoxicity.^[2]

On the other hand, we designed a new magnetic DOX delivery system by growing molecularly imprinted polymers from an individual iron oxide nanoparticle surface (Figure 1b). The magnetic particles covered with the polymer exhibit a cumulative drug release of 60% under AMF compared to 15% without AMF. After internalization in cells, the nanoparticles do not induce cancer cell death demonstrating that when bonded to the MIP (and thus to the nanoparticles), DOX is inactive. By contrast, after AMF application cancer cell viability is affected, with a cell viability reduced to 60% after 1 h30 min treatment.^[3]



Figure 1: a) Magnetic Nanogels and b) Molecularly Imprinted Polymers (MIP) nanoparticles releasing doxorubicin (DOX, in yellow) under an alternative magnetic field (AMF)

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Biological applications of nanoscale Janus particles with dual biofunctionalization

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Janus particles with tailored surface chemistry have been gathering interest for applications as multifunctional cell surface targets, nanomotors and drug delivery systems. Recently, we developed a scalable and adaptive platform for the preparation of nanoscale Janus particles with dual biofunctionality by adapting the established wax-in-water Pickering emulsion strategy.¹ Based on this approach, we designed magnetic Janus nanoparticles which are capable of performing bacterial capture while preventing agglomeration between bacterial cells. Particularly, we prepared silica-coated magnetite Janus nanoparticles functionalized with a bacteria-specific antibody on one side and polyethylene glycol chains on the other. These magnetic Janus nanoparticles selectively interact with one type of bacteria from a mixture of bacteria via specific antigen-antibody interactions. Contrarily to bacterial capture with isotropically functionalized particles, the bacterial suspensions remain free from cell-nanoparticle-cell agglomerates owing to the passivation coating with polyethylene glycol chains attached to the half of the magnetic nanoparticles pointing away from the bacterial surface after capture. Selective magnetic capture of Escherichia coli cells was achieved from a mixture with Staphylococcus simulans without compromising bacterial viability and with a capturing efficiency over 80 %. This approach is a promising method for rapid and agglomeration-free separation of live bacteria for identification, enrichment and cell counting of bacteria from biological samples. Based on these findings, we are currently also investigating similar dual biofunctionalized Janus nanoparticles for use as markers for cell surfaces, both for bacteria and eukaryotic cells.



Figure 1: Janus nanoparticles (gray) with spatially segregated features can be used for magnetic separation of bacteria (green and orange) along with the added benefit of avoiding clustered bacteriananoparticle-bacteria masses during separation. A wide range of tailored functionalizations for specific types of bacteria can be used with the wax-Pickering emulsion method for making gram quantities of Janus particles.

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Hybrid lipid polymer nanoparticles for dual chemo/photodynamic therapy

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Background: Retinoblastoma is a malignant tumor affecting young children. Conventional therapies are associated with severe side effects and may induce secondary tumors. Photodynamic therapy (PDT) is a promising alternative as it is non-mutagenic and induces minimal side effects.^[1] A photosensitizer (PS) is injected to the patient, and the tumor is then illuminated with a laser. The excited PS generates cytotoxic singlet oxygen. The effectiveness of PDT requires the penetration of the photosensitizer into cells. However, most PS are hydrophobic and aggregate in agueous medium. Aim: Incorporation into a nanocarrier may improve PS delivery to the cytoplasm. Furthermore, to treat both the tumor and its seeds, combined PDT and chemotherapy are required. We have designed biodegradable liponanoparticles (LNP) consisting of poly-lactide (PDLLA) nanoparticles coated with a phospholipid bilayer to co-encapsulate an anticancer drug and a PS. Methods: The effective formation of the LNP and their stability was verified by dynamic light scattering, cryo-electron microscopy and fluorescence confocal microscopy. A thorough analysis of the process of adhesion of the phospholipid bilayer onto the PDLLA was performed by combining quartz crystal microbalance and atomic force microscopy experiments, taking into account the properties of the support and the concentration and charge of lipids. Results: This study enlightened the role of charges and polymer mechanical stiffness in the mechanism and kinetics of formation of the liponanoparticles.^[2] The LNP were internalized in retinoblastoma cells within few hours. They showed an improved antitumor activity when the PS and the drug were combined, compared to single therapies. **Conclusion:** LNP are promising nanocarriers for dual PDT/chemotherapy.



PS-LNP in a Rb cell



Figure 1: Liponanoparticles (left) internalized in retinoblastoma cells (right)

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Interaction of Blood Proteins with Polyphosphoesters for Nanocarrier Functionalization

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Nanoparticles and liposomes are used as versatile drug nanocarriers. Upon injection into the bloodstream a protein layer will coat the nanocarrier surface forming the so-called protein corona. This alteration of the nanocarrier surface chemistry induces changes of the drug nanocarrier properties and interfere with the targeting mechanism. In order to prevent non-specific protein adsorption, drug nanocarriers are often coated with protein-repelling polymers. By far the most widely used protein polymer is poly(ethylene glycol) (PEG), but new and more biodegradable polymers such as polyphosphoesters (PPEs) have been recently proposed. It has also been shown that the adsorption of certain proteins can be beneficial and promote specific cellular uptake.

A deeper understanding of protein adsorption to surfaces modified with protein-repelling polymers is therefore desirable to control and guide protein adsorption and orientation. We use monolayers at the air/water interface as model systems for differently functionalized surfaces. We study polymer/water and the polymer/protein interactions by a combination of complimentary surface sensitive techniques. Our results suggest that, for certain proteins, PEG and some PPEs not only influence the amount of adsorbed protein but also the ordering at the surface [1-3] while for other PPEs the interactions seem altogether more complex [2]. These findings will ultimately help in designing new polymers for biomedical applications.



Figure 1: Sketch of the model systems and techniques used in this study.

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Hairy nanocellulose

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Background: The building blocks of cellulose microfibrils, which make up the wall of wood fibers, are cellulose nanofibrils (CNF). These fibrils are several microns long and have a diameter of about 5 nm. They consist of alternating crystalline and amorphous regions, each about 100-200 nm in length. Two forms of nanocellulose can be obtained from CNF: 1) cellulose nanocrystals (CNC), which can be obtained by removing the amorphous regions by acid hydrolysis, resulting in needle-like particles, each about 100-200 nm long and 5 nm wide, which are well studied and presently available commercially; and 2) hairy nanocellulose (HNC), the topic of this talk.

Aim of research: To produce cellulose nanoparticles, while maintaining the amorphous regions. **Methods:** Instead of hydrolysis, we can cleave the chains in the amorphous regions, resulting in cellulose nanoparticles with a crystalline core, with amorphous cellulose chains protruding from both ends. We refer to these particles as hairy nanocellulose (HNC) [1-6]. We can adjust the length of the hairs by acid hydrolysis. A schematic representation of HNC is shown in Figure 1. **Results:** The hairs (i.e. the protruding chains) can be readily functionalized by reactive aldehyde groups, carboxyl groups, quaternary amine groups, and as a result the properties of HNC can be precisely tuned. When charged, they can be readily dried and redispersed, in contrast with CNC, which is difficult to redisperse when dried. We will discuss the synthesis of these particles, their characterization and rheological properties, and point to a number of potential applications, such as heavy metal scavenging, antiscaling agents, antifouling membranes, crystal morphology modifiers, components of wound dressings and when incorporated in carbon nanotubes matrices, they act as a humidity switch.



Fig.1 Schematic representation of hairy nanocellulose (HNC). It consists of a chiral crystalline core of length 100-200 nm and a diameter of about 5 nm, from which chemically modified cellulose chains (the "hairs") are protruding from both ends.

Conclusions: We have developed a novel class of nanocellulose, which can be readily functionalized and which has many potential applications.

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Self-coacervation of polyampholytes: towards biomimetic reactors

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Water-in-water emulsions find their interest in the encapsulation of fragile molecules as the internal and external phases are constituted of water. Typically, all-aqueous phase separation occurs when two water soluble molecules are mixed together. This phenomenon, also called coacervation, has the ability to sequestrate spontaneously various entities from small molecules to complex cells. Self-coacervation is observed when a single type of macromolecule forms micrometric liquid droplets. This process could be assimilated to the coacervation phenomena observed in proteins and constitutes a synthetic model for understanding natural phenomena.

Recently, we have exploited ampholyte polymer chains to create highly stable micrometric drops of self-coacervates, when pH was decreased close to the isoelectric point (Figure 1A).¹ The ampholyte chains are made of a polyanionic chain grafted with cationic groups. We demonstrate that the occurrence of coacervation versus precipitation is driven by the grafting ratio. The resulting coacervates were stable at a given pH but were destroyed by increasing the pH far above the isoelectric point. We propose a soft method to stabilize them even at high pH using calcium ions.

The coacervate droplets present the ability to spontaneously sequestrate a broad panel of entities, from small molecules to macromolecules or colloids, with different charges, size and hydrophobicity (Figure 1 B&C). Thanks to the reversible character of the coacervates, triggered-release could be easily achieved, either by varying the pH or by removing calcium ions in the case of calcium-stabilized coacervates.

These hybrid self-assemblies, compatible with physiological media, find their application in the conception of biomimetic reactors.



Figure 1: A) Optical microscopy image of coacervates. B) Confocal image of rhodamine sequestrated in coacervates. C) Fluorescent images of polystyrene latex sequestrated in coacervates.

Keywords: Water-in-water emulsion, self-assembly, coacervates, sequestration.

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Sculpting Silica Colloids by Etching Particles with Nonuniform Compositions

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Colloids are ideal model systems to study phenomena that occur at the molecular level. When so far centro-symmetrically interacting synthetic colloids were mostly investigated, the interest is currently moving towards complex shapes and interactions. Hereby, particles made of silica are commonly considered for the synthesis of colloids with different shapes, which functionality can be easily modified via surface modification. In this attempt towards more complex but highly defined colloidal particles, we present the synthesis of new shapes of colloidal silica particles obtained by manipulation of their chemical composition and subsequent etching.[1,2] Segments of silica rods, prepared by ammonia catalyzed hydrolysis and condensation of tetraethylorthosilicate were grown under different conditions from polyvinylpyrrolidone loaded water droplets.[3] Upon either decreasing temperature, or increasing monomer concentration. the dissolution rate of the silica segment subsequently formed decreased. An aqueous NaOH solution (~mM) was then used to selectively etch these segments. Further tuning the synthesis conditions resulted in rod-cone or cone-cone shapes particles. Modulating the composition along the particle's length by delayed addition of (3-aminopropyl)-triethoxysilane (APTES) further allowed us to change the composition stepwise. The faster etching of this coupling agent in neutral conditions or HF afforded an even larger variety of particle morphologies besides changing the chemical functionality. A comparable strategy was applied to silica spheres. Biamine functional groups used in a similar way as APTES caused a charge inversion during the growth, resulting in the formation of dumbbells and higher order aggregates. These particles etched more slowly at the neck, resulting in a biconcave silica ring sandwiched between two silica spheres, which were separated by specifically etching the functionalized laver using HF.



Figure 1: Segmented silica rods. The degree of condensation was varied in steps during growth by changing the temperature and reactant concentration. The segments etched differently depending on their degree of condensation.

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Multipoint lock-and-key assembly of golf ball-like particles

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Colloidal modeling which reproduces atoms or molecules in colloidal scale is a useful method for visualization of condensed matter physics with a microscope. Lock-and-key structures of colloids that are combination of dented particles (lock particles) and spherical particles (key particles) have been proposed to create colloidal assemblies [1,2]. The lock-and-key structures can be fabricated by depletion interaction attractively acting between the lock and key particles in the presence of non-adsorbed molecules called depletants [3].

The aim of the present work is to develop multipoint lock-and-key structures of colloids for resembling complex or high-molecular-weight molecules such as branched polymers and proteins. In order to create the structures, golf ball-like particles having multiple dents on their surface [4,5] and spherical particles of which size is almost the same as that of the dents are designed as building blocks (Figure 1). The golf ball-like particles were connected with each other at a spherical particle which acts as a joint in the presence of depletants. The number of golf ball-like particles in a particle assembly depended on the concentration of depletants. Multipoint lock-and-key structures of the golf ball-like particles were created in a highly concentrated depletant solution, resulting in the formation of branched colloidal assemblies. Because the golf ball-like particles and spherical particles were not completely fixed in the solution, the branched assembly exhibited a flexible motion as shown in Figure 2. The colloidal assemblies of golf ball-like particles can be a promissing model for complex polymers in observable scale.



Figure 1: STEM images of golf ball-like particles and spherical particles.



Figure 2: Snapshots and schematic diagrams of particle assemblies.

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Multi-responsive Azopyridine-modified Poly(N-isopropylacrylamide) Colloids in aqueous Solution

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Like azobenzene,¹ AzPy undergoes a photo-induced trans to cis isomerization, followed by a cistrans thermal or photoisomerization. The presence of the pyridine rings enriches the photophysical properties of AzPy, in particular in aqueous media because of its dual light/pH sensitivity. We prepared Az-Py poly(N-isopropylacrylamides) (PNIPAM) of varying molar mass by RAFT polymerization of NIPAM in the presence of a chain-transfer agent that contains an AzPy group and an n-dodecyl chain (C12).² Light scattering measurements, ¹H NMR spectroscopy diffusion and fluorescence probe studies indicate that the polymers self-assemble in neutral water to form colloidally-stable nanoparticles. Transient absorption spectroscopy measurements revealed that the cis to trans thermal relaxation of AzPy is extremely fast in both acidic and neutral dispersions.



Figure 1: pH-Dependent morphology of C12-PNIPAM-AzPy colloidal particles (from 2)

The fast dynamics in neutral pH were attributed to the formation of H-bonds between AzPy and surrounding PNIPAM amide hydrogens. Thus C12-PN-AzPy do not form typical core-shell flower micelles, but adopt a more complex morphology (Figure 1, center). In acidic solutions, the presence of the azopyridinium end group offers various means to adjust the phase transition temperature of the PNIPAM fragments. This study provides new strategies to prepare multi-responsive colloids and fast-responsive light-driven systems.

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Emulsion Droplets Stabilized by Amphiphilic Janus Regular Polygonal Particles

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In Pickering-Ramsden emulsions a liquid-liquid (or gas) dispersion is stabilized with a dense layer of colloidal particles at the interface. The nature of the particle layer thus plays an important role in the property and functionality of the emulsions. Recently the effect of particle anisotropy on the emulsion states has attracted attentions of researchers: Amphiphilicity, a chemical anisotropy, of a particle can make the emulsions not only kinetically but also *thermodynamically* stable [1]. Anisotropy in particle shape is strongly related to the particle arrangement at the interface and thus to the behaviour of emulsions [2]. The anisotropy studied so far is, however, still limited especially in experiment, and its fundamental roles is to be elucidated.

In this contribution we produced plate-like amphiphilic Janus particles with regular polygonal shapes, and experimentally study the effect of the two types of anisotropy, amphiphilicity and shape, on the self-assembled structures in water-in-oil emulsions [3]. The particles exhibited geometric features of regular polygons in (curved) plane filling. The triangular, square and hexagonal particles showed tessellation at the surface of large water droplet respectively (Fig. 1a). When a droplet is small, the triangular, square and pentagonal particles form regular tetrahedral, cubic and regular dodecahedral particle shell respectively (Fig. 1bc). The formation of these characteristic structures were suppressed with the particles without amphiphilicity.

These results demonstrate the essential role of the chemical and geometric anisotropy of the particles in the structures of Pickering-Ramsden emulsions, contributing to designing their functionality *via* the anisotropy.



FIG. 1 Self-assembled structures of amphiphilic regular polygonal particles in water-in-oil emulsions. The scale bars are 10 μ m.

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Identification of ternary composition regions and functional evaluation of bicelles containing intercellular lipids

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Background The stratum corneum intercellular lipids (SCIL), such as cholesterols and ceramides, play an important role in the barrier function of the skin. Stabilizing SCIL into skincare products and getting them to penetrate the skin is challenging because of their high crystallinity. **Aim** Phospholipid vesicles, such as liposomes, are an effective means of penetrating the SCIL [1]. However, it is difficult to stabilize high concentrations of SCIL using vesicles. We addressed this problem by using bicelles. Specifically, we investigated the most appropriate concentrations and ratios of three components (phospholipid, sterol surfactant, and cholesterol or ceramide) to generate bicelles. We then evaluated the functionalities of these bicelles in penetrating SCIL.

Method Polyoxyethylene (POE) cholesteryl ether (10 or 20 E.O.) and phytosteryl ether (10, 20, or 30 E.O.) were used as sterol surfactants. Bicelle structures were characterized by measuring their particle diameter, and by structural observations using a transmission electron microscope (TEM). Their functionality was evaluated by assessing their skin permeability and structurally analyzing their coating films using small angle X-ray scattering.

Results Our results revealed that the phospholipid/POE cholesteryl ether (10 E.O.)/cholesterol ternary system forms four regions: where only vesicles exist (A), where vesicles and bicelles coexist (B), where only bicelles exist (C), and where only micelles exist (D) (Fig. 1,2).

The phospholipid/POE phytosteryl ether (30 E.O.)/ceramide-ternary system was also examined and found to support bicelle formation over a limited region. Furthermore, we observed that ceramide-containing bicelles penetrate the SCIL and form coating films comprising two-lamellae structures coating the skin.

Conclusion We succeeded in preparing bicelles that stably incorporate cholesterol and ceramide. These bicelles are a highly promising and effective approach for both delivering their components to the skin, and to subsequently occlude the skin.



Figure 1: Ternary diagram of phospholipid (PL)/ cholesteryl ether (CS-10)/cholesterol (Cho).



Figure 2: TEM images of three of the four regions (region A, B and C).

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An environmentally benign antimicrobial nanoparticle based on a silver-infused lignin cores

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Silver nanoparticles have antibacterial properties, but their use has been a cause for concern because they persist in the environment. Here, we show that lignin noparticles infused with silver ions and coated with a cationic polyelectrolyte layer form a biodegradable and green alternative to silver nanoparticles. The polyelectrolyte layer promotes the adhesion of the particles to bacterial cell membranes and, together with silver ions, can kill a broad spectrum of bacteria, including Escherichia coli, Pseudomonas aeruginosa and quaternary-amine-resistant Ralstonia sp. Ion depletion studies have shown that the bioactivity of these nanoparticles is time-limited because of the desorption of silver ions. High-throughput bioactivity screening did not reveal increased toxicity of the particles when compared to an equivalent mass of metallic silver nanoparticles or silver nitrate solution. Our results demonstrate that the application of green chemistry principles may allow the synthesis of nanoparticles with biodegradable cores that have higher antimicrobial activity and smaller environmental impact than metallic silver nanoparticles.

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Multifunctional PEG-carboxylate copolymer coated nanomagnets for biomedical application

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Magnetic nanoparticles (MNPs) having inherent unique features for combined use in diagnosis and therapy (theranostics), are in the focus of scientific interest. However, the bare nanoparticles should be coated by multifunctional protective layer to avoid the undesired processes in vivo. Accordingly, we demonstrate a novel way to elaborate a biocompatible shell on magnetite NPs step by step, starting from simple acrylic acid (AA) and PEG to the chemical coupling of PEG chains with carboxylates. New type of functionalized PEG-polymers was synthesized, where the number of anchoring groups and the length of PEO blocks are optionally variable parameters. The functional groups were quantitatively characterized by potentiometric acid-base titrations. Infrared spectroscopy (ATR FT-IR) showed that chemical bond forms between nanomagnet's surface sites and COOH groups. Dynamic light scattering and electrophoresis studies revealed that the chemically attached PEG-polymers influence the aggregation of MNPs depending on the amount of added molecules and their chemical composition. The presence of free carboxyls in the PEG-copolymer shell around the MNPs led to enhanced colloid stability and salt tolerance (>150 mM NaCl) even at physiological pHs. Hemocompatibility (blood sedimentation, peripheral blood smears, white blood cell viability) and cytotoxicity (MTT, Prussian blue staining) tests proved that the superhydrophilic PEG-chains in the protective layer of MNPs can avoid the undesired processes like non-specific protein adsorption or adhesion on cell membranes. The remarkable r_2 value (425 mM⁻¹s⁻¹) from MRI measurements at 1.5 T and the SAR data (9.5 W/g, at 16.5 mT and 330 kHz) from magnetic hyperthermia studies indicates the notable theranostic potential of the new PEGylated MNPs carrying free carboxyls for further capping of various drugs or biomolecules.



Figure 1a) TEM image of coated MNPs, b) Stabilization effect of PEG-polymer, c) Heat production of coated MNPs within the tumour

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Synthesis of biodegradable heteroclusters for targeted drug delivery based on Poly lactic-co-glycolic acid nanoparticles

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Cancer represents one of the most common diseases that affects human health and this has been a constant drive towards finding new approaches to fight it. Over the years, chemotherapy became the standard method to treat cancer. However, it provokes severe side effects. Free chemotherapeutic drugs have the limitation to reach the site of action with an efficacious dose because of its distribution to healthy organs and tissues ^[1]. In this context, targeted therapies have received considerable attention due to their ability to minimize the side effects. To construct nanocarriers-based targeted drug delivery, biodegradable polymers have been employed thanks to their biodegradability and biocompatibility. Poly lactic co-glycolic acid (PLGA) is one of the most successful used biodegradable polymers for drug delivery, thanks to its tuneable properties and possibility to graft binders for targeted delivery ^[2]. Besides encapsulation of a drug, it is interesting to achieve delivery of different compounds as magnetic nanoparticles, which can work as contrast agents and/or for local increase of temperature triggered by magnetic field. The present work consists of the preparation of various types of nanoparticles, i.e. PLGA by nanoprecipitation^[3] and iron oxide by co-precipitation, and their assembly into heteroclusters via electrostatic interactions. Different types of oppositely charged coatings are applied on the surface of PLGA and iron oxide nanoparticles (alginate, polyethyleneimine, chitosan, etc), for cluster assembly. To keep the size of final clusters below one micron, vortexing or sonication was applied during their preparation. Encapsulation of a model molecule, i.e. dye nile red was performed. Encapsulation efficiency was determined by UV-Vis and fluorescence microscopy. The distribution of the dye inside the nanoparticles was visualized by confocal microscopy. This approach represents an easy and reproducible method for production of heteroclusters that can deliver different types of nanoparticles.



Figure 1: Freeze-dried PLGA-ALG coated nanoparticles (left), and cluster of PLGA-ALG/PLGA PEI nanoparticles (right). PLGA-PEI coated nanoparticles look similar to ALG coated nanoparticles.

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Porphyrin Adsorption by Stabilized Titania Surfaces

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Dye sensitized solar cells (DSSCs) based on TiO2 have been studied as an easy to produce, low-cost alternative to classical semiconductor solar cells for a long time [1]. The use of porphyrin molecules as dye in the last years led to DSSCs with efficiencies of up to 13% [2]. We synthesized tunable titania nanoparticles with a diameter of \sim 2-3 nm using a hot injection method [3]. The produced nanoparticles are stabilized by oleic acid. Special emphasis of our work is focused on the exchange process of the oleic acid with porphyrins designed for a particular application.

This process is studied using a variation of scattering techniques. Combined small angle x-ray and neutron scattering (SAXS and SANS) experiments give detailed information on the core/shell structure of the nanoparticles (cf. Figure 1a). The UV/Vis spectrum of porphyrins is very sensitive to changes in conformation and can be used to give additional information on the exchange process (cf. Figure 1b) [4]. Lastly X-ray reflectivity measurements can be used to study the exchange of oleic acid with porphyrins on TiO₂ Wafers as a test system (cf. Figure 1c). From previous experiments we could determine the stabilization layer on top of the nanoparticles

as well as observe the exchange of stabilizing molecules. In the talk an overview over the combination of the different techniques will be given. Furthermore their usage in the characterization of the morphology of the produced particles and the ligand exchange from oleic acid to porphyrins will be presented.



Figure 1: Overview of techniques used for the characterization of the exchange process of oleic acid with porphyrins on anatase nanoparticles: a) Simultaneous fit to SAXS and SANS data of TiO2 nanoparticles; b) UV/Vis spectra of metallated and non metallated porphyrin; c) XRR measurements of Rutile Wafers coated with oleic acid and porphyrin

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Exceptionally Small Organic Nanoparticles: The Internal Structure of Coenzyme Q10 Droplets prepared by Antisolvent Precipitation

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The preparation of organic nanoparticles (NPs) by antisolvent precipitation (AP) represents a promising low-cost alternative to energy-consuming and invasive top-down methods.^[1] However, the impact of AP on the NPs properties is not well understood and no recipe for the production of very small particles (sizes below 30 nm), which are desirable for e.g. pharmaceutical applications,^[2] yet exists.

Here, we report on exceptionally small and stable coenzyme Q10 (Q10) NPs prepared by AP with and without a stabilizer as well as their structural characterization by photon correlation spectroscopy (PCS), differential scanning calorimetry (DSC), cryogenic transmission electron microscopy (Cryo-TEM), wide-angle X-ray scattering (WAXS), and small-angle X-ray and neutron scattering (SAXS, SANS).

The Q10 NPs exhibit sizes down to less than 20 nm and are stable for at least 16 months even without added stabilizer. Strikingly, the combination of SAXS and contrast variation SANS on amorphous SDS-stabilized Q10 NPs revealed an unexpected internal molecular arrangement in which Q10 molecules contribute to the stabilization of the NP dispersion (cf. Figure 1).^[3] This is the first report of Q10 acting as a co-stabilizer, and likely the Q10 molecules contribute to an ordered interface structure of the NPs even when no stabilizer is added to the dispersion. We will present our latest results on the stabilization of these Q10 NPs.



Figure 1: Data (dots) and simultaneous fits (lines) of SAXS and contrast variation SANS (using different H₂O/D₂O ratios and protonated/deuterated SDS) of SDS-stabilized Q10 NPs (left), a schematic representation of the particles based on SAXS/SANS analysis (middle) and the number-weighted particle size distribution derived by Cryo-TEM, PCS, and SAXS/SANS analysis (right).

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Synthesis of porphyrin-conjugated confeito-like gold nanoparticles

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Gold nanoparticles (AuNPs) possess the characteristic of both inertness and biocompatibility which have a great medical application in the biosensor and drug delivery. In biomedicine, this unique optical property can be exploited for application such as phototherapy as well as porphyrin.

Confeito-like AuNPs conjugated with porphyrin were synthesized and characterized in order to clarify the property, especially, singlet oxygen generation towards phototherapy, since singlet oxygen is a key reactive oxygen species responsible for phototherapy.

Confeito-like AuNPs were prepared by the reduction of gold precursor in the presence of citric acid [1]. The conjugation of porphyrin was performed by covalent binding using L-cysteine and carbon dots-protected iron oxide ($Fe_3O_4@C$) as adapted linkages. Singlet oxygen generation can be determined by recording the emission intensity decrease of fluorescent probe (anthracene) in photoluminescence spectra, because the fluorescent probe is turned into non-fluorescence after being oxidized by singlet oxygen.

The binding of thiol group of L-cysteine to confeito-like AuNPs and also the formation of amide bonding between porphyrin and L-cysteine were confirmed by FT-IR spectroscopy, UV-vis spectroscopy, transmission electron microscopy, etc. Additionally, $Fe_3O_4@C$ was formed the amide bonding between confeito-like AuNPs and porphyrin and this product was also characterized as well. Singlet oxygen is greatly important for the application in phototherapy and also indicates itself the effectiveness as a photosensitizer. Confeito-like AuNPs had a great aptitude for singlet oxygen generation but the conjugation of porphyrin on them improved the efficiency of singlet oxygen generation.

This study confirmed the ability of porphyrin-conjugated confeito-like AuNPs higher than confeito-like AuNPs and porphyrin in singlet oxygen generation for phototherapeutic application.

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Avoiding degradation of upconverting nanoparticles in aqueous media by using hydrophobic polymer shells

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Upconversion nanoparticles (UCNPs) are being currently studied due to their ability to emit radiation at a shorter wavelength than they are excited. Furthermore, they present good stability and low toxicity and for these reasons UCNPs are an excellent material in fields such as bioimaging or design of biosensors. The biological applications require UCNPs to be dispersible in polar solvents as water and the aqueous buffer used in biological systems [1]. Over the years, different techniques have appeared to coat the surface of the UCNPs and thus disperse them in water. An example of this is the coating with a silica shell or the use of amphiphilic polymers. However, luminosity loss can occur upon high dilution of UCNPs, even when using partially protecting coatings [2]. The objective of this study is to obtain polymer-coated UCNPs that do not lose luminescence when they come into contact with water or commonly used buffers, paving the way for their use in biological applications.

In this work, NaYF₄ UCNPs doped with Yb^{3+/}Er³⁺ were synthesized using the thermal coprecipitation method. Afterwards, the UCNPs were coated with hydrophobic polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) using a miniemulsion polymerization approach. The transmission electron micrographs in Fig. 1 show: the as prepared monodisperse UCNPs (Fig. 1A); the nanoparticles coated with a layer of PS&PMMA (Fig.1B); and the same nanoparticles as in Fig.1B after the thermal treatment (Fig.1C). The objective of the present study is to analyse the stability of the coated UCNPs after their high dilution in water or buffer, as a function of temperature (25°C, 60°C and 90°C) and time of immersion in the solvent, by measuring their luminescence intensity and lifetime.



Figure 1: Results obtained by TEM. A). NaYF₄:Yb³⁺/Er³⁺. B)NaYF₄:Yb³⁺/Er³⁺@PS&PMMA. C) NaYF₄:Yb³⁺/Er³⁺@PS&PMMA after 10 cycles of temperature (25-60°C) at a concentration of 10 μg/mL.

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Versatile core-shell particles formed by electrostatic complexation between polyampholytes and anionic or cationic surfactants

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This work reports on the use of diblock polyampholytes to prepare water-dispersible core-shell nanoparticles by electrostatic complexation with either anionic or cationic surfactants. For this purpose, poly(acrylic acid)-*block*-poly(2-(dimethylamino)ethyl methacrylate) (PAA-b-PDMAEMA) copolymers with different block lengths have been synthesized and characterized. In these copolymers, the presence of negative charges in the PAA block and positive charges in the PDMAEMA block can be controlled by the solution pH. To explore the versatility of these polyampholytes. we have prepared core-shell particles with either cationic (hexadecyltrimethylammonium bromide (C₁₆TABr)) or anionic surfactants (sodium dodecyl sulfate (SDS)). For the particles prepared with $C_{16}TA^{\dagger}$ and the copolymer $PAA_{24}-b$ -PDMAEMA₅₆, the average hydrodynamic diameter is 260 nm and the surface charge is positive. According to Small Angle X-ray Scattering (SAXS) analyses, the particles core display a hexagonal crystalline structure, which is confirmed by Cryo-TEM images. This result is in good agreement with similar systems previously prepared with anionic-neutral copolymers by our group.^[1] However, when the copolymer PAA₄₁-b-PDMAEMA₁₄₂ is used, the particles display an amorphous core, possibly because of the competition between the long PDMAEMA block and the surfactant to interact with the PAA block. The particles formed by the SDS surfactant display a negative surface charge and hydrodynamic diameters of 110 and 140 nm respectively with the copolymers PAA₂₄-b-PDAMEMA₅₆ and PAA₄₁-b-PDMAEMA₁₄₂. In both cases, the particles display a hexagonal internal structure. These results confirm that is possible to form core-shell particles with ordered structures with both cationic and anionic surfactants using the same polyampholyte. Experiments to reverse their structures by interchanging surfactants are being conducted. In addition, the presence of a charged outer block opens up varied possibilities for use of these nanoparticles.^[2]

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Morse-Witten theory of liquid drops, bubbles and foams

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The theory of Morse and Witten [1], which has wide applicability to liquid drops, bubbles and foams, has hardly found any applications until very recently. Hoehler and Weaire [2] have sought to rectify this, by providing a detailed review of the theory and its potential, in relatively simple terms. It has since been applied (*inter alia*) to 2D and 3D foams [3,4,5], pendant drops [6] and bubbles in square tubes [7]. In foams, it provides an accurate description close to the wet limit, in terms of forces between contacting bubbles, which act between representative points. However, these are not the simple pairwise forces often used in heuristic models. For any given bubble the distortion at each contact depends on all the contact forces, that is, the theory is essentially non-local.



Simulation of a foam using the Morse-Witten theory for bubble-bubble interactions [4]. The simulation is for 100 bubbles (using periodic boundary conditions) and a liquid fraction of 0.13, close to the wet limit (liquid fraction 0.16). The bubbles are shaded according to their individual excess energy. Also shown is the corresponding network of all the contact forces.

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Advective flow in nanostructured bijels via electroosmosis

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Particle stabilized bicontinuous emulsions (bijels) have been introduced over 10 years ago.^[1] Soon after their discovery, their future use as continuously operated crossflow reactors for chemical reactions between immiscible reactants was proposed (Figure 1). This potential yet remains to be demonstrated. Here, we take a significant step towards realizing this vision by introducing advective flow in bijels via electroosmosis. Recently, we have introduced Solvent Transfer Induced Phase Separation (STrIPS), a straightforward technique for generating bijel fibers with asymmetric oil/water channels of micrometer dimensions.^[2] Our current work has advanced STrIPS to generate bijel fibers with submicron sized oil/water channels of high uniformity. Surface tension and contact angle measurements are employed to rationalize the structure formation mechanisms. The uniform channels are found to enhance the mechanical strength and elasticity of STrIPS bijels, as determined by microfluidic in-situ mechanical testing. ^[3] Last, we investigate electroosmotic flow by monitoring dye propagation within the bijel fibers. Electroosmotic flow with speeds of up to 1 cm per minute is observed in the bijels by increasing the voltage and the nanoparticle surface charge. We report our research as a major step towards employing bijels as media for multiphasic processes with potential applications in Pickering interfacial catalysis and as cross-flow microreactors.



Figure 1: Structure of a bijel with arrows indicating advective transport with oil and water channels.

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Bottom-up formation of nanoemulsions by using a flow-reactor mimicking deep-sea hydrothermal vents

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A novel continuous process for making nanodroplets, called monodisperse nanodroplet generation in quenched hydrothermal solution (MAGIQ), will be presented.¹ The process utilizes a unique property of water at high temperature and high pressure near the gas/liquid critical point ($T_c = 374$ °C, $P_c = 22.1$ MPa), where oil and water free mix.^{2,3} In MAGIQ, homogeneous solutions of oil in supercritical water is first prepared, and then quenched to room temperature to induce rapid phase separation, during which nano-sized droplets are formed. MAGIQ is entirely different from conventional top-down emulsification processes in that oil droplets are formed in a bottom-up manner, by self-assembly of oil molecules.

The process is realized by a high-temperature and high-pressure flow-type instrument (Figure 1). In a test using dodecane and a nonionic surfactant, polyoxyethylene(10) oleyl ether (Brij97), as an emulsifier, oil-in-water nanoemulsions containing fine droplets of dodecane, 60 nm in diameter, was obtained in just 10 sec. Thermal degradation of dodecane was less than 1 %, primarily because the residence time with which dodecane was exposed to high temperature only briefly (less than 5 sec). Our laboratory-scale flow-type instrument can produce ~1 L of nano-emulsions per 1 hr.



Figure 1: Flow-type instruments for producing nanoemulsions by MAGIQ

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Spontaneous Ouzo nanoemulsions co-exist with pre-Ouzo aggregates Sylvain Prévost¹, Isabelle Grillo¹, Sebastian Krickl², Werner Kunz², Olivier Diat³, Thomas Zemb³

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Even in the absence of surfactants, polymers or particles, remarkably stable emulsions can be formed spontaneously without energy input by dilution only. Industrial applications of this "Ouzo effect" ^[1] range from food to pharmaceuticals. Spontaneous emulsification is observed when diluting from a domain where dynamic nanometer-sized aggregates are present. Why Ostwald ripening is not effective as destabilizing mechanism accelerating creaming remained unknown. Using in-situ auto-dilution, we followed by Small-Angle X-ray Scattering (SAXS) over more than three decades in reciprocal space the morphological changes occurring when going through the ternary phase diagram water-ethanol-octanol, from the alcohol binary to the water corner. This allows for the first time a full characterization of the multiple-scale coexisting microstructures. Synchrotron-SAXS data were complemented by Small Angle Neutron Scattering (SANS) profiles at particular compositions to benefit from isotopic contrast variation.^[2]

The aqueous phase is an ultra-flexible microemulsion^[3,4] with nanometer-sized polydisperse clusters as confirmed by Molecular Dynamics (MD) simulations^[5]. In the metastable regime, when the Ouzo effect leads to the formation of large droplets, *coexisting phases are both ternary solutions structured at nanoscopic scale*. The oil-rich, micrometer-sized droplets contain up to 30 % water by mass and *are always structured at nanoscale when the emulsion is stable*.

The phase transition is asymmetric around the plait point. When the initial concentration of hydrotrope is below the minimum hydrotrope concentration (MHC), the emulsification fails: emulsions cream immediately because the oil-rich domain does not exhibit direct clusters, only a reverse network. Beyond the MHC, the low surface tension between coexisting ternary fluids that both scatter with an Ornstein-Zernike contribution results in Laplace pressures below 100 Pa, driving towards macroscopic phase separation and explain the puzzling emulsion resilience against the universal mechanism of Ostwald ripening.



Figure 1: Left: ternary phase diagram with the biphasic area, plait point, tie-lines, and localization of the MHC and Ouzo regions. Right: illustration of the small-angle scattering data obtained in the Ouzo region, showing two length scales: the contribution from µm-sized droplets, and that from nm-sized clusters.

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Nanostructures, faceting, and splitting in nano- to yocto- liter liquid droplets

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Contrary to everyday experience, where all liquid droplets assume rounded, near-spherical shapes, the temperature-tuning of liquid droplets to faceted polyhedral shapes and to spontaneous splitting has been recently demonstrated in oil-in-water emulsions[1]. However, the elucidation of the mechanism driving these surprising effects, as well as their many potential applications, ranging from faceted nanoparticle synthesis through new industrial emulsification routes to controlled-release drug delivery within the human body, have been severely hampered by the micron-scale resolution of the light microscopy employed to date in all *in situ* studies[1-2]. Thus, the thickness of the interfacially frozen crystalline monolayer, suggested to drive these effects, could not be directly measured, and the low limit on the droplet size still showing these effects remained unknown.

We employed a combination of super-resolution stimulated emission depletion microscopy, cryogenic transmission and freeze-fracture electron microscopy, to study these effects well into the nanometer length scale, employing hexadecane oil droplets, stabilized in water by a common cationic surfactant, octadecyltrimethylammonium bromide. We demonstrate the occurrence of the faceting transition in droplets spanning an incredible 12 decades in volume from nanoliters to yoctoliters[3]. We directly visualize the interfacially-frozen, few nanometer thick, crystalline monolayer[3] which drives these effects[1] (Fig. 1). The bulk of the droplets is structureless, ruling out the formation of a surface-adjacent 300 nm - thick crystalline structure, hypothesized in some earlier studies[2] to drive the faceting of the droplets. Finally, our measurements allow placing an upper-limit estimate on the two-dimensional Young modulus of the interfacial nanometer-thick surface crystal in the smallest droplets, providing insights into the virtually unexplored domain of nanoelasticity.



Figure 1: CryoTEM image of the edge of a vitrified faceted droplet. The interfacially-frozen layer, only a few nm thick, is marked by an arrow. No internal structure is visible.

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How gum Arabic stabilizes emulsions: interfacial packing and networking

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Gum Arabic is a natural hydrocolloid harvested from acacia trees, which is extensively used to stabilize concentrated beverage emulsions. Gum Arabic is a complex mixture of covalently linked protein and polysaccharides macromolecules with various size, hydrophobicity and protein content. Large gum amounts are used in formulation (> 10 wt%), leading to depletion and higher costs, which is thought to stem from the low concentration large protein/polysaccharide conjugates. Nevertheless, gum Arabic actually contains a broad array of species that might all reach the interface, calling into question its supposedly shortage of amphiphilic species.

We have conducted a mechanistic study along the following questions: (1) How does gum Arabic structure in solution? (2) What is the interfacial partitioning and packing in emulsions stabilized by gum Arabic? (3) What is the structure of the oil/water interface in the presence of gum Arabic? We used a combination of two chromatographic separations, an interfacial-mediated separation, and SAXS and SANS characterizations in solution and in emulsions to answer these questions.

We show that protein-rich species are preferentially adsorbing at oil/water interfaces. Yet, these species actually display a broad array of structures and thus sizes. While the interfacial composition thus significantly differs from the bulk one, it is not very sensitive to formulation parameters such as pH or salinity. However, we observed drastic variations in the interfacial packing or coverage upon varying these parameters. We also showed that large interfacial packings promoted the irreversible formation of hydrophobic networks at oil/water interfaces. We evidenced that such networks relate to emulsion metastability, which suggests an original mechanism based on the amplification of steric repulsions by an elastic network. These findings can be directly transposed to rational formulation, and allow to divide by an order of magnitude the amount of gum Arabic used, while remaining the same emulsion metastability.

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Symmetry break in emulsion droplets of mixed alkanes upon cooling

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Medium- and long-chain alkanes and their mixtures possess a remarkable property – they form intermediate structured phases between their isotropic liquid phase and their fully ordered crystal phase.^[1] These intermediate phases are called "rotator phases" because the alkane molecules have long-range positional order while preserving certain mobility to rotate. Significant expansion of the domain of rotator phases existence is observed for mixtures of alkanes as compared to the individual alkanes.^[1] The rotator phases were invoked to explain the mechanisms of two recently discovered phenomena in cooled alkane-in-water emulsions – the spontaneous "self-shaping" and the spontaneous "self-bursting" of emulsion drops.^[2,3] Experimentally, the "self-shaping" phenomenon is observed when oily drops are dispersed in solutions of appropriate long-chain surfactant and are slowly cooled down to temperatures around the freezing point of the oil. Upon such cooling, the drops break symmetry, transforming consecutively from spheres, to fluid polyhedra, hexagonal, tetragonal or triangular platelets, and finally – to thin long fibers.^[2,4]

The current talk presents results from a systematic study of the ability of drops containing mixed alkanes to deform upon cooling.^[1,5] The observed trends are summarized as follow: (1) The general drop-shape evolution for multi-component drops is the same as with single-component drops, however, some additional shapes are observed; (2) Preservation of the particle shape upon freezing is possible for alkane mixtures with chain length difference $\Delta n \leq 4$, for greater Δn – phase separation within the droplets is observed; (3) Multi-component particles prepared from alkanes with $\Delta n \leq 4$ plastify upon cooling due to the formation of a bulk rotator phase within the particles; (4) If a compound, which cannot induce self-shaping when pure, is mixed with a certain amount of a compound which induces self-shaping, then mixed drops can also self-shape upon cooling. These results demonstrate that the drop self-shaping and the formation of rotator phases are very typical for multicomponent alkane-in-water emulsions.



Figure 1: (a) Drop shape evolutionary scheme observed upon cooling. (b-d) Fluid nonspherical drops, prepared with different oil mixtures and stabilized by various surfactants: (b) hexagonal platelet; pentade-cylcyclohexane : eicosane = 1:2 v/v, $C_{18}\text{EO}_{20}$. (c) tetragonal platelets; heptadecane : heptadecene = 1:1, $C_{18}\text{SorbEO}_{20}$. (d) triangular platelet, hexadecane : dodecanol = 1:1, $C_{18}\text{SorbEO}_{20}$. Scale bars, 20 µm.

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Controlling foam ageing in viscoelastic media

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Foams are dispersions of gas bubbles in a continuous medium. Their typical cellular structure lends them lightness and peculiar mechanical properties that are exploited in many industrial applications.

However liquid foams are only meta-stable systems. After their generation, a competition between different mechanisms alters the foam structure over time. Drainage, coalescence and coarsening can be a strong limitation in industrial processes, as they slowly lead to an irreversible foam damage. The desired longevity of a foam clearly depends on the specific applications, which call for a thorough understanding of foam stability.

We study how the mechanical properties of the continuous phase impact on the coarsening process, in conditions where drainage and coalescence can both be neglected. For this purpose, we use oil-in-water emulsions as the continuous phase of foams. At high droplet concentrations, emulsions can possess a shear rigidity and act like an elastic solid, thanks to the storage of interfacial energy from droplet deformations. We study foamed emulsion coarsening in 3D samples using diffusing-wave spectroscopy and in pseudo-2D foams.

We show that emulsion viscoelasticity allows to study foam coarsening at constant liquid fraction, as the foam drainage and coalescence are negligible during the time scale of the experiments.

We also show that increasing emulsion elasticity influences the ripening of foamed emulsions: if the emulsion is very elastic the coarsening process slows down dramatically.

The results can lead to a more efficient control of the foam structure and stability.



Figure 1: example of a foamed emulsion seen under the microscope.

Stabilising effect of wax crystals on oleofoams under varying temperature

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Oil foams, or oleofoams, which are dispersions of gas bubbles in a continuous oil phase, are common in the food industry as well as the oil and gas industry. Recently, crystals of fatty acids/alcohols or edible waxes have been found to provide stability and extend the applicability of oleofoams in aerated formulations. There is evidence that the stabilisation is due to the adsorption of crystals onto the bubble interfaces by the so-called Pickering mechanism. Because the excess crystals remaining in the continuous oil phase form an oleogel, an effect of the bulk rheological properties is also expected. In addition, these systems are extremely sensitive to temperature, because heating can melt the crystals, while cooling at different rates results in the formation of different crystal polymorphs. Here, we evaluate the contributions of bulk and interfacial rheology below and above the melting point of a wax forming an oleofoam in sunflower oil. We study the dissolution behaviour of single bubbles using video microscopy on a temperature-controlled stage. To assess the different rheological contributions, we compare the behaviour of a bubble embedded in an oleofoam and a bubble extracted from the oleofoam and re-suspended in oil. In the first case, the bubble owes its stability to both bulk and interfacial rheology, while in the second case the contribution of the interfacial dilatational rheology alone can be observed. We find that below the melting point of the wax, bubbles in the oleofoam are stable whereas bubbles that are only coated with wax crystals dissolve. Both systems are unstable against dissolution when heated above the melting point of the wax. These findings are rationalised through independent bulk rheological measurements of the oleofoam and oleogel at different temperatures, as well as interfacial rheological measurements of the wax-coated interface using drop shape fitting elastometry.

Foams of Vegetable Oils Containing Long Chain Triglycerides

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Oil foams are scarcely investigated despite their prevalence in the food, cosmetics and petroleum industries. Contrary to aqueous foams, the fabrication of oil foams is difficult due to limited adsorption of surfactants at the air-oil interface. Herein we describe a simple protocol to produce edible oil foams with excellent stability from neat vegetable oils containing long chain triglycerides without any additive or emulsifier.

Upon cooling from the melt or warming from the gel, crystals of high-melting triglyceride (TAG) form within the continuous phase of low-melting liquid, thereby forming a crystal dispersion or oil gel. These mixtures can be whipped to produce oil foams stabilised by TAG crystals. Optimum foaming gave an overrun of around 40 % for refined peanut oil and 110 % for extra virgin olive oil. Oil foams without drainage, coarsening or coalescence were prepared where the bubble surfaces were covered by crystals and excess crystals served to gel the bulk phase. Ultra-stable oil foams also exhibited thermo-responsiveness, and could be rendered unstable when heated to around the melting point of the TAG crystals.

Stability and rheology of protein foams: contribution of interfacial properties, involvement of film relaxation dynamics

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The stability and flow properties of surfactant-stabilised aqueous foams are keys to their use in various application contexts. The main destabilisation processes in aqueous foams are liquid drainage, coalescence and disproportionation. They behave as yield-stress fluids, in which flow leads to film-scale topological rearrangements known as T1s.

Still, the contribution to these features of the properties imparted by the surfactants to the airliquid interface is far from fully understood.

Proteins are amphiphilic macromolecules. They lower the air-water surface tension, as small-molecular-weight surfactants do, but in contrast with the latter, they adsorb irreversibly to the interface and give specific interfacial visco-elasticity.

In order to correlate the stability and rheology of protein foams to the properties of interfaces, we adopted a multi-scale approach combining the interfacial rheology, the dynamics of foam films after T1 topological rearrangements, and macroscopic foam characterisations: the foam stability against drainage was evaluated by following the evolution of the liquid fraction as a function of both time and height in the foam column^[1], and the foam complex modulus and yield stress were measured under oscillatory shear. We investigated the behaviour of dairy proteins (whey protein isolate or purified β -lactoglobulin), either in the native state or after modification by dry-heating and/or pH adjustment prior to dehydration, to vary interfacial properties.

Our results show that small-extent structural modifications of proteins had a dramatic impact on interfacial rheology, liquid film dynamics, foam stability and foam rheology.

This approach, correlating multiple investigation scales, sheds light on the contribution of the interfacial rheology to protein foam properties, in particular through the involvement of film relaxation dynamics.

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Effect of Surface Phase Transition on OW Emulsion Stability

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Penetration of alkane molecules into the adsorbed film gives rise to a surface freezing transition of cationic surfactant at the alkane-water interface upon cooling. In this study, we utilized the surface freezing transition of cetyltrimethylammonium chloride (CTAC) at the tetradecane-water interface to stabilize oil-in-water (OW) emulsions. When the oil-water interface was in the surface liquid state, the OW emulsion prepared at the critical micelle concentration of CTAC coalesced readily and the volume of OW emulsion decreased to 1/3 within 24 hours whereas the OW emulsion was stable in the surface frozen state and a conspicuous volume change was not observed. The stability of OW emulsion occurred in a first-order manner at 9.5 °C which almost matched the surface phase transition temperature determined by interfacial tensiometry and ellipsometry. A mechanical hindrance to droplet coalescence due to the surface freezing transition was considered as a plausible reason of the emulsion stabilization.



Figure 1: Pictures of OW emulsion samples prepared with the surface liquid film (15.0 $^{\circ}$ C) and surface frozen film (7.0 $^{\circ}$ C) and height of emulsion phase plotted as a function of time (b).

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Emulsions, Pickering Emulsions & Foams EMUL2-7 Polyelectrolyte Capsules Containing Water-in-Water (W/W) Emulsions

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Water-in-Water (W/W) emulsions are dispersions of one aqueous phase into another aqueous phase [1]. These emulsions can be prepared in aqueous two-phase systems where phase segregation occurs by thermodynamic incompatibility between two hydrophilic components [2]. Therefore W/W emulsions are formed without oil and without surfactant. It is known that these emulsions can be stabilized by particles adsorbed at the W/W interface [3,4]. These fat-free emulsions can be highly interesting for food and drug delivery applications.

In the present work, Water-in-Water emulsions were introduced in the interior of capsules. W/W emulsions were prepared with an anionic polyelectrolyte (either sodium alginate, NaAlg, or sodium carboxymethyl cellulose, NaCMC), mixed with a globular protein (bovine serum albumin, BSA). These two combinations showed phase separation, and their phase behaviour was studied. Stable BSA-in-Alg and BSA-in-NaCMC emulsions were produced and characterized. These W/W emulsions were introduced inside capsules, by coacervation with Ca^{2+} or Fe^{3+} (illustrative example in Fig. 1).



Fig. 1. Capsules and macroporous interior of a freeze-dried capsule.

Freeze-drying was used to obtain dried capsules with a smooth surface (made of polyelectrolyte-cation complexes) and a highly porous interior (formed by the presence of W/W emulsion droplets). These porous capsules might have interesting applications in encapsulation of active components and various possibilities are being evaluated.

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Functionalised silica particles showing clouding behavior provide controllable phase inversion in Pickering emulsion systems

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Understanding, and controlling, the phase behaviour of particle-stabilized (Pickering) emulsion systems can expand, and facilitate, the use of these surfactant-free emulsions in industrial applications. Βv surface function-alization with methyl poly(ethylene) glycol (mPEG) silane we are able to provide surface active silica nanoparticles (SiNPs) with a pH dependent and controllable flocculation temperature. behavior^[1] and also a clouding behavior (Figure



Figure 2. SiNPs functionalized with mPEG silane display reversible clouding upon increasing temperature.

2)^[2]. By attaching an additional hydrophobic group, such as a propyl silane to the SiNP surface, we find that these particles, functionalized with both propyl and mPEG silanes, become useful as emulsion stabilizers^[3]. By exploiting the increasing hydrophobicity exhibited by PEG-chains at increasing temperature, phase inversion is achieved in butanol emulsions, where an inversion from o/w to w/o is observed at elevated temperatures (Figure 1). Both the clouding phenomena and the phase inversion temperature (PIT) are affected by the pH and the salt concentration, due to interparticle, intramolecular and salting out effects, as well as the PEG-silica interaction.



Figure 1. Pickering emulsions, with butanol as oil phase, stabilized by SiNPs functionalized with propyl and mPEG silane, undergo phase inversion upon increasing the temperature during homogenization. Left: Conductivity of the emulsion system, as a function of emulsion temperature. When the system is cooled while still homogenizing, the emulsion switches back to the initial state, o/w, with a hysteresis effect ΔT . Right: Microscope images of butanol emulsions. Depending on pH, salt concentration and heating conditions, different systems are obtained.

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Pickering emulsions by thermoreversible attachment of colloidal particles in binary mixtures

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Emulsions play an important role in everyday life and can be found in, for example, food, paints and cosmetics. They consist of two immiscible liquids where one liquid is dispersed in the other liquid. Although emulsions are thermodynamically unstable, they can be kinetically stabilized by the addition of surface-active agents, e.g. surfactants or solid particles. Particle-stabilized emulsion, so-called Pickering emulsions, have enhanced stability as compared to emulsions stabilized by surfactants.^[1] Furthermore, the use of solid particles allows for the formation of environmentally friendly emulsions. The preparation of an emulsion requires the formation of interfacial area, often induced by applying a high shear.

We create interfacial area by temperature-induced phase separation of a binary mixture. These partially miscible liquids have a lower and upper critical solution temperature. Below the lower and above the upper critical solution temperature, the liquids are fully mixed. However, between the two critical solution temperatures, phase separation occurs. To prevent full phase separation, we add colloidal particles to the binary mixture. These particles tend to adsorb at the newly created interface, thereby forming solid-stabilized emulsion droplets. This allows for a temperature-induced formation of Pickering emulsions.

At temperatures significantly above the critical temperature, we observe that coalescence of the solid-stabilized droplets does not occur. In that situation, the temperature-dependent adsorption energy is strong enough for the particles to attach irreversibly which is not the case close to the critical solution temperature. However, Ostwald ripening still leads to an increase in the average droplet size. We study the influence of additional components that preferentially dissolve in droplets, thereby enhancing the stability of the emulsion against Ostwald ripening.^[2]



Figure 1: Formation of a Pickering emulsion from partially miscible liquids by increasing the temperature above the critical temperature.

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Pickering emulsions stabilized with gold, magnetite and silica nanoparticles

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Pickering emulsions with nano- and microparticles can be stable to coalescence and creaming if a gel-like network of aggregated particles is formed in a dispersion medium of emulsions. In this work, stability of emulsions with gold/silica and magnetite/silica nanoparticles was investigated experimentally and by mathematical modeling using Langevin dynamics method. Simulation experiments were carried out with silica, gold and magnetite nanoparticles with diameters of 12, 20 and 70 nm, respectively; oil droplets were 1 µm in diameter.

Results showed that initially chain-like heteroaggregates of silica and gold nanoparticles attached to the surface of oil droplets (Fig. 1a). Over time these heteroaggregates shrank. The oil droplet surface was covered with bulky protruding structures of aggregated silica and gold nanoparticles. The aggregates that were not attached to the oil droplets consisted of a small number of nanoparticles and had a non-elongated form. These heteroaggregates did not combine to form a gel-like network in the aqueous phase of emulsions, so such emulsions were unstable to creaming. However, bulk heteroaggregates on the surface of oil droplets prevented them from approaching and fixed droplets at some distance from each other. This was in agreement with experimental results. The aqueous phase partly separated from emulsions with silica and gold nanoparticles. The oil phase fraction increased in the residual emulsion, but was less than the dense packing of droplets.

Emulsions stabilized with Ludox CL and magnetite nanoparticles were stable to creaming and coalescence. Silica and magnetite nanoparticles aggregated with the formation chain-like heteroaggregates that were located in the volume of the aqueous phase and attached to the surface of oil droplets (Fig. 2b). The data obtained using mathematical modeling corresponded to experimental data. Emulsions stabilized with magnetite and silica nanoparticles at pH 8 were stable to coalescence and creaming for a long time.



Figure 1: Snapshots of oil droplets (green) stabilized with nanoparticles. Gold, magnetite and silica nanoparticles are red, orange and yellow, respectively

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Responsive Microgels at Interfaces: Influence of Temperature on the Monolayer Properties

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Microgels are deformable, soft, three-dimensional crosslinked polymer networks, typically spherical shaped, in the size range between 0.5 to 10 μ m and swollen in a good solvent.[1] Their stimuli-responsiveness allows the realization of smart emulsions, which can be broken on demand.[2] However, their interfacial properties and demulsification mechanism are not fully understood. In our study, we aim to elucidate the connection between their temperature-dependent swelling (i.e. softness) and properties at liquid-liquid interfaces.

We synthesized thermo-responsive poly(*N*-isopropylacrylamide) p(NIPAM) microaels and measured their interfacial properties at temperatures below (20 °C) and above (40 °C) their volume phase transition temperature (VPTT). At these temperatures microgels lower the interfacial tension of water-decane interfaces to values below 20 mN/m. A Langmuir-Blodgett trough was used to investigate the mechanical properties of the microgel monolayer, with subsequent deposition to a substrate. The deposited microgels were recorded ex situ with atomic force microscopy (AFM). This allows the translation of compression isotherms from area per mass to area per particle (A_p) . With respect to the swollen microgels, the compression isotherms at T = 40 °C show a one-staged course (Figure 1 left). By image analysis we found structurally identical phases for both states, yet the transitions take place at different compressions and the microgels above the VPTT at high surface pressures become incompressible. The combination of Langmuir-Blodgett trough experiments and ex situ AFM (Figure 1 left) demonstrate that the microgel area at the interface is nearly temperature independent. However, with ellipsometry (Figure 1 right) we prove that the microgel volume situated in the aqueous phase is still thermoresponsive.

As a consequence, at elevated temperatures the microgels collapse in the out-of-plane direction and the monolayer becomes denser, leading to distinctly different mechanical properties. Our findings emphasize the fundamental differences between rigid and soft colloids at liquid-liquid interfaces.



Figure 1: (left) Compression isotherms of surface pressure, π , *versus area per particle*, A_p , at T = 20 and 40 °C. (right) Results of Dynamic light scattering (hydrodynamic radius, R_h) and ellipsometry (monolayer thickness, δ_{ell}) as a function of temperature.

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Fabrication of 3D porous cellulose aerogels by sacrificial templating

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Aerogels are highly porous, lightweight materials that find many applications such as thermal and acoustic insulation, catalysis and oil spill removal. Aerogels based on silica have been extensively studied due to the reliability and scalability of the fabrication process. However, the high cost of silica and the high energy requirements of the fabrication procedure (eg freezedrying) have pushed researchers to look for more environmentally friendly alternatives. Cellulose is a promising alternative as it is cheap, abundant, biodegradable and easy to functionalize^[1].

In this study we present a low cost and sustainable fabrication method that allows use to produce porous cellulose based materials. A dispersion of cellulose microfibrils obtained from plants is mixed with ammonium bicarbonate, a thermally decomposing material that serves as a template. This mixture is then heated to decompose the ammonium bicarbonate, leaving behind a porous cellulose material with densities as low as 0.03 g.cm⁻³. The mechanical properties and microstructure of the obtained aerogels were easily tailored by controlling the concentrations of cellulose microfibrils, template particle sizes and volume fraction.

These results open new avenues for the fabrication of sustainable lightweight materials with tailored properties through surface functionalization or incorporation of other inorganic materials.



Figure 1: Method for ultraporous cellulose preparation by templating dispersion of plant microfibrils with a sacrificial template.

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Differential dynamic microscopy extracts multi-scale activity in complex fluids and biological systems

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Differential dynamic microscopy (DDM) is a technique that exploits optical microscopy to obtain local, multi-scale quantitative information about dynamic samples, in most cases without user intervention. It is proving extremely useful in understanding dynamics in liquid suspensions, soft materials, cells, and tissues. In DDM, image sequences are analyzed via a combination of image differences and spatial Fourier transforms to obtain information equivalent to that obtained by means of light scattering techniques. Compared to light scattering, DDM offers obvious advantages, principally (a) simplicity of the setup; (b) possibility of removing static contributions along the optical path; (c) power of simultaneous different microscopy contrast mechanisms; and (d) flexibility of choosing an analysis region, analogous to a scattering volume. For many questions, DDM has also advantages compared to segmentation/tracking approaches and to correlation techniques like particle image velocimetry. The very straightforward DDM approach, originally demonstrated with bright field microscopy of aqueous colloids [1], has lately been used to probe a variety of other complex fluids and biological systems with many imaging methods. including dark-field, differential interference contrast, wide-field, light-sheet, and confocal microscopy [2]. The number of adopting groups is rapidly increasing and so are the applications. Here, we briefly recall the working principles of DDM, we highlight its advantages and limitations, we outline recent experimental breakthroughs, and we provide a perspective on future challenges and directions [3]. DDM can become a standard primary tool in every laboratory equipped with a microscope, at the very least as a first bias-free automated evaluation of the dynamics in a system.

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Super-Hetrodyne Dynamic Light Scattering for Colloidal Dynamics in the Presence of Moderate Multiple Scattering

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We present a novel approach to MS-free dynamic light scattering to study charged colloidal fluids, crystals and glasses. Super-Heterodyne Dynamic Light Scattering (SH-DLS), accesses $g^{(1)}(q,\omega)$ in frequency space with complete discrimination of MS, low frequency noise and homodyne spectral contributions. Careful restriction of collection volume and scattering vector limits collection of MS-light. Excellent ensemble averaging solves for the non-ergodicity problem in colloidal solids in an elegant way. Samll angle SH-DLS is introduced in some instrumental detail. Applications include the density dependence of electro-kinetic mobilities, flow profiling or self-diffusion studies irrespective of system structure. Future extension to q-dependent measurements is discussed. In summary, SH-DLS promises to become a very versatile tool for the investigation of colloidal dynamics in turbid and/or non-ergodic samples



Figure 1: performance and scope of SH-DLS (from left to right, top to bottom) 1) SH-Spectrum at 30% transmission; yellow: MS contribution [1]. C_{shet} is directly proportional to the Fourier transform of $g^{1)}(q,t)$. No Siegert relation needed. Signal bears information on solvent flow profile, particle diffusion and drift velocity [2]. 2) electro-phoretic and –osmotic mobility as a function of particle concentration [3] (Volume fractions from 10^{-4} to 5 10^{-2} , (F) fluid (C) crystalline). 3) Grain boundary self diffusion during crystallization and coarsening [1]. 4) pumping current of micro-fluidic osmotic pumps for different substrate materials [2]. 5) Double-arm goniometer based SH-DLS. SH employs a 2kHz frequency shift between illumination beam and reference beam. Large beam overlap ensures excellent ensemble averaging [3]. 6) Comparison of D_{exp} from SH-DLS and standard DLS for a single scattering non-interacting sample [3].

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Variable Wavelength Resolution for Neutron Reflectometry at European Spallation Source

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Neutron scattering studies are important to gain insight into structure and dynamics of soft matter. These studies allow to highlight different regions of interest due to a large contrast between hydrogen and deuterium. In particular, neutron reflectometry is used to gain information about a sample composition perpendicular to the surface. The European Spallation source (ESS), the future leading neutron source in Europe located in Lund (Sweden), will provide a large neutron pulse with a high flux. To avoid starting from the scratch at day 1 of neutron flux, the ESS testbeamline (V20) was built up located at the Helmholtz-Zentrum Berlin (HZB, Germany). [1] This offers the possibility to prove instrumentation concepts for ESS. The source beam at HZB is modulated by a set of choppers to mimic the long ESS pulse structure. Therefore, different methods and components can be tested and evaluated for operation at the ESS.

Due to the long pulse structure, the wavelength resolution is above 10% which is sufficient for many purposes. Nevertheless, for some purposes it is necessary to increase the resolution. Especially for large structures, it is important to measure with high resolution. Therefore, wavelength frame multiplication (WFM) [2] is used to increase the wavelength resolution below 2%. Here, the source pulse is cut into 6 sub-pulses and stitched afterwards.

The concept of WFM and its influence on neutron reflectivity measurements will be presented. For comparison reflectometry measurements are carried out both at V20 and at V6 reflectometer (HZB) at the same samples. At V20, variable resolutions are generated by using different pulse shapes. The data reduction as well as some benchmarks will be presented. Additionally, advantages of the new concept and their benefits for interface science at future ESS beamlines will be demonstrated.

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Effective Interactions and Dynamics of Active Colloids in Phase Separating Medium

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Janus colloids suspended in phase separating critical liquid mixtures have been used to realize model active colloids [1]. An active motion is initiated with the onset of the phase separation of the solvent mixture. To gain a deeper understanding of the mechanism behind this active motion, we have investigated the evolution of interparticle interactions and dynamics of silica and silicanickel Janus colloids in guasi-binary mixtures of 3-methylpyridine (3MP) and heavy water/water (W). The partial structure factor of colloid interactions and intermediate scattering functions describing the particle dynamics were simultaneously obtained using ultra-small angle X-ray Scattering and X-ray photon correlation spectroscopy. A multi-speckle analysis allows dissecting the evolution of interactions and dynamics in vertical and horizontal direction. Here phase separation is induced by a rapid temperature jump from the one-phase to the two-phase region. Near the critical point of the solvent mixture, the phase separation occurs via spinodal decomposition while in the off-critical mixtures by nucleation and growth or spinodal decomposition depending on the magnitude of the temperature-jump. Static interactions showed a clear difference between silica and Janus particles [2, 3]. The former displaying little change of interactions since the aggregating region is rapidly bypassed during the temperature-jump. Janus particles instead tend to aggregate into clusters which partly re-disperse manifesting the dynamic clustering feature. The dynamics of the bare silica is completely governed by the advection of colloids to the 3MP phase. Velocity fluctuations gradually decay with the coarsening of the phases. Whereas Janus particles display velocity fluctuations initially but they were rapidly suppressed by the dynamic clustering. The general behavior seems to be similar whether the phase separation occurs via spinodal decomposition or by nucleation and growth but differences arise in the onset and decay rate of the velocity fluctuations. As expected, the decay rate of velocity fluctuations is also proportional to the magnitude of the temperature-jump with nearly isotropic dynamics.

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Measurement of volumetric size distribution of nanofluids by Laser Extinction Spectroscopy

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During the last decades, nanofluids gained particular scientific interest because of the large variety of potential applications in material technology, biomedical and electronic fields. Although it is clear that phenomena such as particle aggregation strongly modify nanofluid properties, there is a lack of measurement techniques which can be implemented in situ and in real time to monitor the effective particle size distribution (PSD) and concentration of nanofluids.

The scope of this work is to show that by using the "Light Extinction Spectroscopy" (LES) technique, it is possible to determine the volumetric PSD and the aggregation rate of the SiC-water nanofluid. Therefore, the technique can be used for in situ monitoring of aggregation. The LES is based on the extinction of a collimated broadband light beam passing through a medium containing nanoparticles. Due to nanoparticles, the light intensity attenuates, and this depends on its wavelength, relative refractive index of the particles to the medium, shape and size of the particles, and concentration. Then, the modelling of the transmitted light spectrum is obtained by the Lorenz-Mie light scattering theory, and the volumetric PSD is retrieved via Tikhonov regularization inversion algorithm (see Figure 1a).

We will present numerical simulations proving the feasibility of the LES to monitor nanoparticle aggregation in fluids. The advantages and the limitations of the technique will also be highlighted. Finally, experiments performed in a micro-cuvette (see Figure 1b) filled with SiC-water nanofluid will be demonstrated, showing the nanoparticle aggregation and sedimentation. The results are then compared to models reported in literature and will be considered as a proof of concept.





Figure 1: (a) Synthetically generated lognormal distribution (red circle) and retrieved distribution by the LES (black square) (b) Experimental setup

Experimental Techniques

EXP1-6 Optimizing the printing image – Analysis of the ink and substrate surface properties under inkjet conditions"

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Compatibility of ink and substrate is crucial for an optimal printed image. Currently in inkjet printing, the ink must be adjusted to each printer head and then precisely formulated for the printing process. Consequently the only degree of freedom for desired print image lies in the properties of the substrate's surface. By choosing a proper substrate or modifying it, according to its surface free energy, the required wettability and adhesion properties can be obtained; sometimes even without any primer or additional sealing process, which reduces production costs. Further to wetting and adhesion, the absorption process on absorbent substrates has an influence on the final image quality.

With the optical contour analysing system OCA 200 (Dataphysics) we analysed the wettability of different raw and modified substrates by contact angle measurements and determined their surface free energy. With this knowledge it was possible to estimate wetting and adhesion behaviour of inks.. Using the picodrop dosing system PDDS together with the OCA 200, we furthermore observed the ink-substrate interaction directly under inkjet drop dispensing conditions. We could determine contact angle changes due to absorption and wetting with a speed of up to 1 ms.. . As small quantities of ink (~100 μ l) already allow the evaluation of thousands of drops with the PDDS it can easily be used for early stage printing tests of newly developed ink formulations with conditions similar to the inkjet process and thus without the risk of printer head blockage. These measurements enable fast and reliable determination of the surface properties of substrates and inks which finally simplifies the choice of substrate-ink combination for ideal image printing. Selected examples will be presented within this talk.

Dynamical characterization of worm-like micelles through advanced light scattering technologies.

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There is significant research interest in the field of soft matter that focuses on studying slow relaxation processes in systems that are close to a phase transition or are dynamically arrested. Gels, glasses and aging soft materials are example of such systems. In some cases, accessing dynamic properties in time scales of seconds or even minutes is crucial.

One method that allows for studying slowly relaxing systems is to perform many DLS measurements, to obtain time averaged correlation functions. Between each measurement the sample is rotated such that a different speckle is observed. The results are then averaged to provide the ensemble average ^[1]. Additionally, when working with concentrated samples, the suppression of multiple scattering is required to obtain meaningful results. This is achieved through the 3D modulated cross-correlation technique ^[2,3], where two temporally separated light scattering experiments are performed at the same scattering vector on the same sample volume in order to extract only the single scattering information common to both.

In this work, we present modulated 3D static and dynamic light scattering (SLS and DLS) measurements on Polystyrene particles suspended in a matrix of worm-like micelles. Using a sample goniometer, we rotate the sample to record a subsection of the configuration phase space. We then average over many sub-ensembles to capture the full phase space. Additionally, the middle and high frequency rheology of the system is measured via DWS microrheology.

We demonstrate that to follow such systems undergoing dynamical relaxation, as well as to study dynamically arrested samples, modulated 3D cross-correlation combined with a sample goniometer is a perfectly suited experimental tool that can record information otherwise not accessible.

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Relating nanostructure to macroscopic properties using a laboratory Rheo-SAXS setup

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Rheology deals with the flow and deformation of matter; it relates a material's molecular structure to its mechanical properties. Applying mechanical force, e.g., shear to a material can result in orientation of molecular assemblies or crystallization.

Small-angle X-ray scattering (SAXS) determines structural parameters of nanostructured materials: size, shape, inner structure and orientation. Relating the nanostructure of a material to its macroscopic mechanical properties requires *in-situ* characterization techniques such as rheology combined with SAXS.

Rheo-SAXS experiments have so far been conducted only at synchrotron beam lines, mainly due to insufficient X-ray flux of laboratory X-ray sources and the lack of a dedicated Rheo-SAXS laboratory set-up.



Figure 1: Rheo-SAXS set-up

One experiment that in particular benefits from this development are in-situ Rheo-SAXS measurements. The integrated Rheo-SAXS sample stage enables temperature-controlled rheological experiments with *in-situ* determination of shear-induced structural changes of nanostructured materials on a nanoscopic length scale (from approx. 1 nm to 200 nm) by small-angle X-ray scattering.

In this contribution we present new results of experiments on combined Rheo-SAXS studies with the SAXSpoint 2.0 laboratory SAXS system. With a newly designed optical setup of the SAXSpoint 2.0 the overall flux of SAYSpoint 2.0 instrument could be further increased to more than 5 x 10^8 ph/s. This opens up the way to a variety of new experiments with excellent data quality in minimum time.

Near wall velocimetry and slip of viscoelastic dispersions

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High concentration colloidal dispersions form viscoelastic materials that often yield when sheared. The evolution of viscoelasticity during the yielding process leads to large variation of the near wall flow and in particular of variation of near wall velocity and slip.

The ability to probe near wall velocimetry of complex fluids is needed to establish a complete understanding of the flow of the dispersions. Total internal reflection and its evanescent wave provide a mean to probe the dynamics within microns of the interface when combined with dynamic light scattering. We apply evanescent wave dynamic light scattering (EWDLS) in situ on commercial rheometers to probe near wall velocimetry [1] under well controlled shear stress. The use of rheometer offers a broad range of shear stress, the EWDLS covers a large range near wall velocity (from 100 nm/s to 10 mm/s) providing a large slip length range (from few 10s of nm to mm).

We report on the technique and its use to establish the relationship between the near wall slip and stress in yielded suspensions including concentrated suspensions of microgels or hard spheres. At very low shear rate, the un-yielded materials present very large slip lengths. When yielded, the dispersions show small finite slip lengths (of the order of 100nm). The slip length is monitored at very low shear rates following a yielding pre-shear, together with the applied shear. The slip length is observed to increase with time as the elasticity of the dispersion reforms and the applied stress increases.

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AC electrophoretic mobility of a single colloidal particle studied by holographic video microscopy

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Electrophoretic mobility has been widely used to evaluate the zeta potential of individual colloidal particles, which governs the stability of colloidal dispersions. The mobility under DC electric field is frequently measured by Light scattering, electro-kinetic sonic amplitude method or direct tracking by video microscopy. In this study, we demonstrate two experimental methods to measure AC electrophoretic mobility μ of a micron-sized single particle at 0.5 Hz- 500 Hz by tracking its three-dimensional position using holographic video microscopy^[1].

An interference image (hologram) of scattered and direct light from the particle by irradiation of collimated light emitting diode (LED) is measured by video microscopy^[2] as shown in Fig. (a). The three-dimensional position of the particle is estimated using optical diffraction theory^[3]. For the simplicity of analysis, we reconstructed a three-dimensional optical field from the hologram by Rayleigh-Sommerfeld back-propagation (RS) method^[2]. Fig. (b) shows an example of three-dimensional trajectory of a particle undergoing electrophoresis in a planar electric field.

In a planar electric field setup, the height dependence of the measured value of μ in the cell enables us to evaluate the actual value of μ , by remove of the interference from electroosmotic flow. In a vertical setup, the true value of μ can be directly evaluated by minimizing the influence of the electrode polarization, using a thick cell and a high-frequency electric field. The estimated values of μ obtained using both methods agree with that from conventional electrophoretic light scattering. We also evaluated the distribution of μ values within a colloidal dispersion.

The merits of this method over conventional one is its applicability to multi-particles' system where their holograms overlap and the particles of fast sedimentation.



Figure: Holographic microscopy of a carboxylated polystyrene microspheres of 1.9 μ m diameter in water undergoing electrophoresis.

(a)Hologram of a particle.

(b)3D-trajectory of a colloidal sphere settling down with Brownian motion under AC electric field (167 V/m, 0.5 Hz).

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Small-angle neutron scattering and in situ UV/Vis absorption spectroscopy of photoresponsive wormlike micelles

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The ability to observe chemical processes simultaneously with small-angle scattering is highly desirable for a deeper understanding of biological and soft matter systems. This is particularly crucial for dynamic systems, to ensure sample stability, purity, chemical conditions, and for where it is not possible to perform further measurements or characterisation on intermediate states *ex situ*. However, while such environments are becoming almost mainstream at large scale X-ray sources, they remain rare at neutron facilities.

Consequently, as a part of a larger sample environment development project at KWS-2 at the Jülich Centre for Neutron Science, which already includes *in situ* dynamic light scattering and Fourier infrared spectroscopy, we have recently developed a set-up for *in situ* UV/Vis absorption spectroscopy and light irradiation. A proof-of-concept investigation was undertaken to provide mechanistic and kinetic insights into the photoisomerization and self-assembly of a novel photoresponsive azobenzene-containing surfactant (AzoPS), see Fig. 1.^[1] It was shown that the incorporation of spectroscopy with SANS allows the scattering profile, and hence micelle shape, to be correlated with the extent of photoisomerisation in real-time. This combined UV-Vis/SANS approach could be extended to various other systems to allow monitoring of their self-assembly process, where the only requirement is the presence of a characteristic absorption spectrum.



Figure 1: Self-assembly behaviour of AzoPS in D₂O upon *trans-cis* photoisomerisation.

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Growth kinetics of bimetallic nanoparticles followed by *in situ* techniques

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Surface plasmon resonances of noble metal nanoparticles can be modulated by tuning the particle morphology (size, anisotropy, edge roundness) or by covering them with a different metal^[1]. It is however difficult to follow this complex process, due to the lack of unintrusive *in situ* techniques. An important challenge in the field is to correlate *in situ* single particle monitoring with other techniques in which the particles are produced in different conditions.

We follow the seeded growth of Au-Ag core-shell noble metal particles by small-angle X-ray scattering, by UV-Vis absorbance spectroscopy and by environmental transmission electron microscopy (ETEM) in liquid cell. The results are correlated with *ex situ* measurements performed on quenched aliquots extracted from the reaction medium.



Figure 1: a) Series of ETEM images (10 s apart) of the growth of the silver shell onto a gold bipyramid; b) superellipse fits to the particle outlines; c) time evolution of the major and minor axes as well as the "bluntness" index *n* deduced from a revolution *superellipsoid* model: $(r/a)^n + (z/b)^n = 1$, where $r^2 = x^2 + y^2$ is the radial distance and z the height. Parameters *a*, *b* and *n* are shown for one particle evolution in Figure 1c.

We will discuss the influence of the various parameters on the kinetics and the final shape of the particles^[2]. We will also show that using several complementary methods to follow the same system during its evolution yields a more detailed and reliable picture of the process than any one technique taken separately.

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Structure and Dynamics of Polyelectrolyte/Microemulsion Complexes (PEMECs) Controlled by Polyelectrolyte Type and Droplet Charge

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By admixing polyelectrolytes (PE) to charged oil-in-water microemulsion droplets one can form polyelectrolyte/microemulsion complexes (PEMECs), where colloidal stability and structure are controlled by the properties of the individual components. In our experiments we varied systematically Mw and type of the polyelectrolyte as well as size and charge density of the microemulsion droplets and determined the phase behaviour (see Fig. 1) and structure by means of static and dynamic light scattering, small-angle neutron scattering and cryo-TEM. Interestingly the phase behaviour depends mainly on the Mw of the polyelectrolyte but little on its type. In contrast the mesoscopic structure as seen by SANS and cryo-TEM depends markedly on all system parameters.

In our study we employed microemulsion droplets where the positive charge was controlled by the percentage of cationic surfactant contained in the surfactant mixture and as complexing polyelectrolytes sodium polyacrylate (NaPA), hydrophobically modified NaPA, carboxymethylcellulose (CMC), and hyaluronate (HA). With increasing Mw larger complexes are built and they become more rod-like with increasing stiffness of the polyelectrolyte. The strength of interaction is controlled by the type of polyelectrolyte and the charge density of the droplets and polyelectrolyte which can be controlled by pH, as both the polyelectrolytes and the main surfactant (alkyl amine oxide) are pH responsive in the pH range of 4-9. Accordingly these are systems, where the structure can be tuned largely via the composition and pH. Further dynamic experiments with PFG-NMR and neutron spin-echo (NSE) showed a remarkably high internal dynamics of these systems. In summary, PEMECs are an interesting and so far only little explored colloidal system that on one side serves is a well-defined model system for fundamental investigations and at the same time is highly relevant for microemulsions formulations for cosmetic or pharmaceutical applications, due to their loading with hydrophobic components.



Figure 1: structural phase diagram of PEMECs as a function of charge percentage of the polyelectrolyte (z = [-]/([+] + [-])) and Mw of the sodium polyacrylate employed here.

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Adsorption process makes microgels either behave as flexible polymers or colloids

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PNIPAM microgels are thermo-responsive and combine the properties of flexible polymers and hard colloids. Depending on the cross-linker amount incorporated in the microgel network one of these characters is dominating.^[1] In addition, microgels are highly interfacial active, even though not being amphiphilic. The adsorption to the interface is accompanied by microgel deformation, due to a balance between the maximization of the adsorption energy and the restriction by the elasticity of the network.^[2,3]

We studied two very different microgels in terms of cross-linker content, (i) 5 mol% cross-linked, and (ii) ultra-low cross-linked (ULC) PNIPAM microgels. The collapse in bulk solution of these microgels is similar as shown by static light scattering (SLS) and small-angle neutron scattering (SANS) measurements. However, atomic force microscopy (AFM) measurements revealed that the confinement of the microgels at the solid interface leads to strongly different behaviors. While 5 mol% crosslinked microgels always collapse into smooth half ellipsoids, the ULC microgels do not have one equilibrium collapsed morphology. The final balance between adsorption energy and network elasticity can be trapped in two different states, depending on the adsorption process. On one hand, the polymeric character is dominating when ULC microgels are deposited via spin-coating and only single polymer chains collapse into globules, whereas on the other hand, the directly adsorbed ULC microgels are restricted in their deformation and collapse into homogenous half ellipsoids as regularly crosslinked microgels. By tuning the adsorption process, one and the same microgel can be used to obtain strongly different surface topographies.



Figure 1: AFM height images of the same ULC microgels collapsed at a solid interface, but adsorbed via two different pathways; spin-coating (left) and direct adsorption (right).

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IMAG1-4

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Mapping the layer-thickness of thin films on curved surfaces is still a scientific as well as technical issue, especially in the field of colloid and surface science,

Here, we present a generalized approach for the calculation of the Mueller-Matrix of a tilted isotropic sample that overcomes before-mentioned limitations regarding the AOI. We apply our model in order to extract the sample parameters N,C,S (or equivalently Δ and Ψ) from the Mueller Matrix measured on a strongly tilted or curved, but otherwise isotropic sample.



This approach proves to be particularly powerful for the application of Imaging Mueller-Matrix Ellipsometry (IMME) to the characterization of curved surfaces (Figure 1). A single IMME measurement yields a map of the (local) ellipsometric Δ - Ψ -values regardless of different local normal vectors within the field of view and without any need to realign the sample for different spots on the surface.

Core/shell colloids as ideal model systems to study photothermal heating in dilute dispersion

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Noble metal nanoparticles such as gold or silver support localized surface plasmon resonances (LSPRs).[1] The absorbed energy of this resonant excitation of collective oscillations of the valence electrons is typically dissipated non-radiatively, i.e. by heat. Consequently plasmonic nanoparticles can be used as local, nanoscale sources of heat. This in turn is interesting to locally trigger phase transitions, for example, of phase change materials or thermoresponsive polymers.[2] Ideal model systems to study photothermal heating, its influence on the volume phase transition of a thermoresponsive polymer and on particle diffusion, are core/shell colloids with single, absorbing nanoparticle cores and thermoresponsive polymer shells.[3]

We use angle dependent pump-probe dynamic light scattering (PP-DLS) to study the nonequilibrium Brownian motion of core/shell colloids during laser-heating. The colloids contain single, spherical gold nanoparticle cores that are homogeneously encapsulated in thick, thermoresponsive hydrogel shells. The size of the gold cores is adjusted to provide a strong spectral overlap between their LSPR and the wavelength of the pump laser. Intermediate scattering functions (ICFs) were recorded from dilute particle dispersions using the scattered light of a probe laser that operates at a center wavelength where absorption by the colloids is negligible. Simultaneously the samples are illuminated with the pump laser to excite the colloids nearly at resonance. With increasing pump power the recorded ICFs increasingly deviate from single exponentials and become stretched (fig. 1, left). Detailed analysis of the particle motion reveals a transition from normal diffusion at zero pump power to superdiffusion for high pump powers (fig. 1, right). This effect is related to a pronounced photothermal heating. Furthermore we show that this heating event leads to a shrinkage of the thermoresponsive hydrogel shells.[4]



Figure 1: Left: ICFs of Au-PNIPAM core/shell microgels recorded at pump laser intensities of 0, 0.5 and 2.2 W. The solid lines represent cumulant fits and the dashed lines fits using strechted exponential decay functions. Right: MSD as a function of relaxation time.

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Structure and Dynamics of Clay Particle Dispersions

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Clay particles are used as additives for many different purposes be it as viscosity modifiers, as flame retardants, for low gas permeability, or for scratch resistance. The high aspect ratio of the platelets supports all those material improvements. Very often, the fundamental understanding of platelet dispersions is at the beginning when it comes to theoretical descriptions of the structural and dynamical properties. These concepts are highly desired when it comes to the next generation of products with even higher performance.

Scattering experiments provide the structural and dynamic information that is needed to understand the mechanism of clay particle dispersions. Clay particles dispersed in water and microemulsions show examples of quite low and extremely high viscosities for certain aspect ratios (Fig. 1, left)^[1]. These findings are rationalized by applying a simple viscosity model of membranes in a viscous medium. The principal understanding of low viscosities was transferred to crude oil dispersions where lower viscosities were obtained at low temperatures^[1]. The structure of clay/polymer dispersions was analyzed using medium and wide-angle scattering (Fig. 1, right)^[2]. A simple model rationalized the findings, especially the rather low limit of platelets forming a stack at about 3-4. From all the given simple models, new developments and improvements would be facilitated in the near future.



Figure 1, Left: Complex viscosity of clay dispersions with different diameters for two different media, namely a microemulsion and simple water. Solid lines result from viscosity model for membranes. Right: The medium angle scattering of clay/polymer nanocomposites with model fits: XRD of solvent casted PEO 3350 with LRD (red), bulk PEO 3350 with LRD (blue), average neutron scattering of many PEO molar masses with LRD (black).

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Profiling flocculating and sedimenting particles with position resolved USANS and neutron dark field imaging

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Flocculants are usually polymeric molecules which cause the aggregation of particles in suspensions and will modify the sedimentation of particles. The gravitational field and the hydrodynamics of the aggregates result in a situation where larger aggregates sediment more quickly for less efficient packing and smaller particles will sediment more slowly. Such considerations are important in the formation of filter cakes where the porosity of the structure is critical for the transport of water and the hydraulic conductivity. Here we consider the structural profile of flocculated CaCO₃ particle suspensions under the influence of gravity and a commercial flocculent in the direction of the gravitational field with the aim of an understanding of the packing of particles. Dark field imaging ^[1] provides high resolution imaging of the structures formed by sedimented particles with contrast provided by the arrangements of particles over different correlation lengths. We also consider spatially resolved USANS using the KOOKABURRA instrument ^[2] of the same suspensions after sedimentation which can consider an extended range of length-scales but have limited spatial resolution. The two techniques are complementary providing a detailed understanding of the porosity of the filter cake.

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Imaging, Scattering & Microstructure

IMAG2-2 Light scattering from hollow silica nanocubes: form- and structure factors of hard superball fluids.

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Colloidal cubes form dense crystal phases when their assembly is induced by gravity ^[1] or the depletion interaction ^[2]. Although these crystal phases have been studied in great detail, experimental studies on the fluid properties of colloidal cubes are still lacking. Recently, we developed a method to prepare dispersions of hollow silica nanocubes ^[3] which show longstanding colloidal-stability. Here we present a detailed light scattering study on these nanocubes, including the first measurements of a concentrated stable cube fluid. At low concentrations, contrast variation experiments were used to determine the optical properties of the silica particles. Systematic measurements at finite colloid concentrations allowed for the determination of the osmotic compressibility, which is compared to theoretical results for a hard superball fluid [4].



Figure 1: Left: Static Structure factors obtained from SLS measurements of hollow silica nanocubes. Right: TEM micrograph of hollow silica nanocubes with an average edge length of 125 ± 10 nm.

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Convectively Assembled Monolayers of Colloidal Cubes: Evidence of Optimal Packings

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Colloidal particles under confinement are of interest for various applications, such as photonics, chemical sensing, biomimicry, and solar cells. One of the convenient methods for the preparation of colloidal films on a substrate with precise thickness is controlled solvent evaporation, i.e. convective assembly. Thanks to breakthroughs in colloid synthesis, many types of micron-sized colloids with well-defined anisotropic shapes and interactions are now available. Particle shape can greatly influence the periodic microstructures the colloids assemble into and it is of fundamental and practical interest to study the close-packed structures these non-spherical colloids can form.

Here, we employ a system of cubic colloids with rounded corners and study the effect of the cubic shape on close-packed monolayers that form during convective assembly. We show that large crystalline films of colloidal cubes can be obtained.^[1] Using scanning electron microscopy and particle tracking algorithms we investigate the obtained structures in detail and show that the monolayers possess their predicted densest optimal packings, the Λ_0 -lattice and Λ_1 -lattice,^[2] as well as the simple-square lattice and disordered packings (Fig. 1). In addition, we find that these structures easily transition into each other and contain many different types of defects. We further find that the exact roundness of the cubes corners plays an important role for the final packing symmetry.^[3] As the roundness of the cube corners decreases the frequency of the Λ_1 -lattice increases, while the frequency of the Λ_0 -lattice remains unaffected. The formation of both optimal packings is found to be a consequence of the out-of-equilibrium formation process during convective assembly, which leads to small shifts in rows of cubes thereby transforming the Λ_1 -lattice into the Λ_0 -lattice.



Figure 1: The self-assembly of cubic colloids into monolayers induced by convective assembly shows the formation of different optimal packing symmetries.

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Towards a quantitative prediction of the flow of polydisperse rod-like colloids

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Their vast natural abundance and usefulness for industrial applications makes dispersions of rodlike colloids an important object to study. Of particular interest are the phase behavior and the rheological behavior of suspensions of rods. Despite the broad interest, there remains a lack of understanding of the flow behavior of semi-dilute suspensions of rods, especially in the case of particle flexibility and polydispersity. We used a combination of rheology and in-situ small angle neutron scattering to relate the macroscopic stress to the microscopic 3D orientational ordering [1,2] for a library of monodisperse rod-like viruses. We gained a complete understanding of the pronounced effect of length on the zero-shear viscosity as well as the shear thinning, see Figure 1. Moreover, we showed, using modified viruses, that an increased particle flexibility lowers the zero-shear viscosity and has no marked influence on the shear thinning behavior [3]. We exploited this result to attack the problem of polydispersity. By mixing two species of very disparate lengths to a benchmark bi-disperse suspension, we find that the average particle length determines the flow behavior. Based on the established theoretical approaches [4,5], we developed a new way of reducing the full Yvon-Born-Green cascade of Smoluchowski equations which allows us to quantitatively predict the orientation and stress of rod-like suspensions of different lengths and also of bi-disperse suspensions. With this combined theoretical and experimental study, we approach also full understanding of the flow behavior of polydisperse rods from the dilute up to the nematic liquid-crystalline state.



Figure 1: (a) Reduced shear viscosity and (b) orientational order parameter as a function of the effective Péclet number for Pf1 (L=1.96 μ m), M13k07 (L=1.2 μ m), and Y21M (L=0.91 μ m) at different concentrations reduced to master-plots. Lines are novel theoretical results. The straight line in (a) shows an L⁻¹ dependent viscosity, anticipated for a shear banding fluid.

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Axial electrokinetic trapping of anisotropic particles

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In recent years anti-Brownian electrokinetic trapping has become a valuable tool in the study of colloidal particles and inter-particle interactions in liquid [1,2]. With electrokinetic trapping the diffusion coefficient, electrophoretic mobility, interactions with other particles, alignment and rotation can be analyzed for prolonged times on a particle-to-particle basis. However, axial trapping of particles, especially of anisotropic particles, in micron-scale devices is challenging because of the difficulty to extract the z-position from microscopy images and because of screening of the electric field. In this work, axial electrokinetic trapping of anisotropic particles in water is realized in devices with planar, transparent electrodes [3]. To achieve trapping in the axial direction a trapping algorithm is developed which uses Fourier-Bessel decomposition of standard microscopy images and which is learning from the correlation between applied voltages and changes in the particle appearance. No previous knowledge on the particle appearance, theory fitting or advanced optical setup is required. The algorithm is demonstrated by axially trapping singlets, doublets and triplets of polystyrene particles in water. To characterize the trap strength and to extract particle properties, the motion of a trapped particle is investigated in detail. Analysis of the power spectrum of the particle position reveals a time-dependency of the electric field that is related to the build-up of diffuse double layers at the electrodes. This charge buildup results in screening of the bulk field and Faradaic reactions at the interfaces at higher voltages, which should be taken into account properly in the analysis of particle properties. In conclusion. electrokinetic trapping has been used to axially trap and analyze anisotropic particles. The method can be useful for studying the behavior and interactions of all kinds of complex colloidal systems such as Janus particles and Pickering emulsions at the particle-to-particle level.



Figure 1: a) schematic of axial electrokinetic trapping, and b) image decomposition of a particle triplet which is trapped in the z-direction but otherwise freely rotating.

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On how to study the Microstructure of Gelled Lyotropic Liquid Crystals

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Gelled lyotropic liquid crystals (LLC) combine the mechanical stability of a gel with the microstructure of a LLC. They can be obtained by adding a gelator to a LLC or by replacing the solvent of a gel by a LLC.^[1] We use low molecular weight gelators which form gels via self-assembly. Two questions are examined: (1) Do the gel network and the LLC form simultaneously but independently, i.e. are gelled LLC orthogonal self-assembled systems? (2) Does the chronology of LLC and gel formation influence the microstructure of the LLC and the alignment of the gel fibers?

We study the gelled L_a and the gelled H₁ phase of the system H₂O – C₁₂E₇ (heptaethylene glycol monododecyl ether)^[2] in the presence of the organogelator 1,3:2,4-dibenzylidene-D-sorbitol (DBS)^[3-5]. Varying the DBS mass fraction η , two sol-gel transition temperatures $T_{sol-gel}$ are adjusted: (a) $T_{sol-gel}$ are above the melting points $T_{LLC-iso}$ of the LLCs at η = 0.0075 and (b) $T_{sol-gel}$ are below $T_{LLC-iso}$ at η = 0.015. This allows us to investigate (a) the influence of the gel network on the microstructure of the LLC and (b) the influence of the LLC on the alignment of the gel fibers.

In this contribution, we present small angle x-ray and light scattering as well as transmission electron microscopy which showed that the gel network and the LLC coexist. However, the LLCs influence the gel network independent of the chronology of gel and LLC formation: The gel fibers are bundled as opposed to the binary gel ethylene glycol - DBS for which randomly distributed gel fibers are detected. The gel network has only small influence on the microstructure of the LLCs since the repeat distances are hardly affected. The results are discussed in terms of orthogonal self-assembled systems where two coexisting self-assembled supramolecular structures may or may not interact.

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Segregation in multicomponent droplet evaporation

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While the evaporation of a single component droplet meanwhile is pretty well understood. the richness of phenomena in multicomponent droplet evaporation keeps surprising us. E.g., the evaporation of ternary liquid droplet can lead to spontaneous nucleation of droplets consisting of a new phase [1]. This new phase can be utilized to self-lubricate the droplet in order to suppress the coffee stain effects [2]. In this talk we will show that even in the evaporation of binary droplets very surprising phenomena can occur, namely evaporationtriggered segregation thanks to either weak solutal Marangoni flow [3] or thanks to gravitational effects [4]. To explore the latter, the flow in an evaporating glycerol-water binary submillimeter droplet with a Bond number $Bo \ll 1$ is studied both experimentally and numerically. First, we measure the flow fields near the substrate by microparticle image velocimetry for both sessile and pendant droplets during the evaporation process, which surprisingly show opposite radial flow directions - inward and outward, respectively. This observation clearly reveals that in spite of the small droplet size, gravitational effects play a crucial role in controlling the flow fields in the evaporating droplets. We theoretically analyze that this gravity-driven effect is triggered by the lower volatility of glycerol which leads to a preferential evaporation of water. The emerging local concentration difference of the two components leads to a density gradient that drives the convective flow. We show that the Grashof number Gr is the nondimensional control parameter for the occurrence of the gravitational effects. We confirm our hypothesis by experimentally comparing two evaporating microdroplet systems, namely, a glycerol-water droplet and a 1,2-propanediolwater droplet. We obtain different Gr, larger or smaller than 1, by varying a series of droplet heights, which corresponds to cases with or without gravitational effects, respectively. Finally, we simulate the process numerically, finding good agreement with the experimental results and again confirming our interpretation.

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Towards microfluidic measurements of colloidal dispersions equations of states

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We first report the fabrication of poly(ethylene glycol) diacrylate (PEGDA)-based microfluidic chips, integrating highly permeable nano-porous membranes inside microchannels for the investigation of ultra-filtration processes at the nanoliter scale.

More precisely, after fast prototyping of PEGDA chips, a maskless UV projection device is used to photo-pattern PEGDA-based hydrogel solutions within the channels. This set-up makes possible the polymerization of in-situ membranes with a spatial resolution of a few microns. These membranes withstand transmembrane pressure drops up to several bars owing to their strong anchoring on the chip walls. We also perform in-situ Darcy permeability measurements of these membranes. Permeability can be tuned by adjusting the deposited exposure energy and/or the hydrogel formulation (namely PEG chains playing the role of porogen agents). This methodology [1] allows us to integrate strongly anchored membranes with permeabilities ranging from K = 10 to 50 nm², corresponding to typical porosities I ~ K^{1/2} in the 3 to 7 nm range, in line with ultra-filtration processes.

We are currently using these chips to measure the equation of states of charged colloidal dispersions (e.g. nano-latexes or nano-silica), i.e. the relation between osmotic pressure and colloids concentration. We are indeed able to compress micro-dialysis sacks containing colloids within a micro-channel ended by the nano-porous membrane, see Figure 1. A tangential flow downstream the membrane also imposes the chemical potentials, as the macroscopic tank of usual osmotic compression experiments making use of milliliter dialysis sacks immersed in larger baths. We expect that the small volumes involved in such experiments (typically 0.1 to 5 nL), combined with the possibility of in-situ observations and high throughput screening, will open the way to fast and accurate microfluidic measurements of equation of states of complex fluids, a highly tedious task at macroscopic scale.



Figure 1: Ludox silica nanoparticles dispersion (AS40) within a micro-dialysis sack compressed at a pressure P against a nano-porous membrane. The width of the channel is $120 \,\mu\text{m}$ and its height is $45 \,\mu\text{m}$. The thickness of the membrane is $20 \,\mu\text{m}$.

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Fluorocarbon-assisted microbubbles decorated with dendronized iron oxide nanoparticles for biomedical imaging

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Microbubbles (MBs) are micron size gas particles dispersed in an aqueous medium with an outer shell built from surfactants, phospholipids, polymers or nanoparticles.^[1] Fluorocarbon gases (FCs) are reported as efficient co-surfactant and osmotic agents to stabilize phospholipid-shelled MBs.^[2] FC-assisted MBs are clinically used as contrast agents (CAs) for ultrasound imaging and are investigates as drug delivery systems.^[3] Here we report the preparation of self-assembled bimodal CA based on hybrid perfluorohexane (F-hexane)stabilized MBs with a phospholipid shell that incorporates iron oxide nanoparticles (IONPs) grafted by fluorinated dendrons (Fig. 1a,b) for ultrasound and magnetic resonance imaging. Small (1 µm in radius) and stable (half-time life 4 h) MBs were obtained with a high-shear mixing technique, and investigated by optical microscopy and an acoustic attenuation method (Fig. 1c,d). Adsorption of IONPs onto MBs was supported by atomic force microscopy, which shows that IONPs are embedded in the phospholipid shell (Fig. 1a). The Gibbs film kinetic adsorption studies demonstrated that the F-hexane core plays a significant role in enhancing IONPs adsorption at the gas/water interface due to fluorine-fluorine interactions between Fhexane and the C₂F₅ moieties of the dendron. The magnetism of the IONPs remains unchanged when they are embedded within the MBs shell, as demonstrated by relaxometry investigations. Results of preclinical in vivo ultrasound and magnetic resonance imaging studies on breast cancer mouse model will also be presented.



Figure 1: Schematic representation of a) a *FC* gas-core magnetic microbubble and a dendronized IONP. b) Structure of the dendron fitted with a terminal C_2F_5 moiety. c) Optical microscopy image and d) size distribution of magnetic microbubbles.

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Coalescence of surfactant-laden and surfactant-free drops in microfluidic device

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Droplet-based microfluidics is a quickly developing area of science and engineering enabling study and optimisation of drops and bubble formation and coalescence inside immiscible continuous phase. The promising microfluidic applications include micro-reactors, where chemical reactions or studies on interactions of living sells with various compounds are carried out under well controlled conditions of isolated drops on timescales from milliseconds to days. One of the ways to perform a micro-reaction is bringing together and coalescing two drops containing the reactants. In this case controlled mass transfer between the drops is crucial for the control of reaction kinetics. As the composition of drops is different, the interfacial tension with the continuous phase can also be different. This difference can affect the mass transfer. Here we present the results of an experimental study of the mass transfer accompanying the coalescence of two drops of different composition: one drop is surfactant-laden and another one is surfactant-free. Drop coalescence results in the Marangoni flow directed on the interface from the surfactant-laden to the surfactant-free drop and the bulk flow due to difference in capillary pressure between the drops resulting in penetration of content of surfactant-free drop into surfactant-laden one. These local flows interact with the general flow in microchannel. As a consequence, the mass transfer between the drops depends not only on surfactant properties and concentration and viscosities of continuous and dispersed phases, but also on the flow rate in microchannel, drop confinement and on drops order. In particular the mass transfer is considerably more intensive if the surfactant-laden drop is followed by the surfactant-free one as shown in Fig. 1.



Figure 1: Mass transfer at asymmetrical drop coalescence in microchannel. The (light) surfactant- laden drop is 300 mM solution of C_{10} TAB in water; the continuous phase is silicone oil.

A microfluidic investigation on osmotic transport in multiphase systems

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Figure 1: (a) Nucleation and motion of water droplets inside an oil meniscus separating two aqueous solutions having different solute concentrations in a glass capillary. (b) Expulsion of oil from microcavities by osmosis.

Oil reservoirs have a complex composition including solids, hydrocarbons and salted water. It has been observed that the injection of low salinity water could lead to an increase of the oil recovery efficiency. The overall picture of this phenomenon is not fully understood but two main underlying mechanisms might be at work. First, the wetting properties on the solid walls of the porous medium depend on the aqueous phase composition, in terms of salinity, type of ions or pH, which is thus modified in presence of low salinity water. This modification could lead to a dewetting of the oil from the stone. Second, the oil can act as a semipermeable membrane where water can diffuse through under osmosis due to a salt concentration mismatch. This osmotic flow then leads to a displacement of the oil in the porous network.

Microfluidics is an adapted tool to study the motion of oil in presence of different aqueous phases as it allows to well control geometrical features, wetting properties or liquid compositions of this multiphase system. A first device, built with a glass capillary, allowed us to probe the water transport, and thus oil movement, at the level of a single oil meniscus. Tuning oil properties led to a remarkable phenomenon where nucleation of water in oil droplets accompanied with their motion take place (Fig. 1 (a)). A second microsystem is composed of microcavities that can trap salted water and oil that is expulsed when immersed in a water phase having a low ionic concentration (Fig. 1 (b)). This approach allowed us to shed light on the link between wetting properties, porous medium geometry and osmosis in such an oil recovery context. In addition, the proposed experimental methodology opens the way to an exploration of out of equilibrium phenomena occurring in multiphase systems.

What controls the lifetime of antibubbles?

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An antibubble is a liquid droplet wrapped by a thin layer of gas, inside a bulk usually of the same liquid. The lifetime of an antibubble is governed by the drainage of the gas between the two liquid-gas interfaces populated by surfactants. Depending on the relative magnitude of surface viscosity and elasticity properties, which directly depend or are determined by the nature of surfactants, the lifetime of an antibubble may vary a lot, from few seconds to few minutes [1]. While experimental lifetimes are comparable whatever the dominating property, intrinsic differences exist as revealed by modeling. Nevertheless, these differences were not observed experimentally in previous studies, due to important sources of dispersion. In this work, the main sources of dispersion have been identified, such as (i) the initial amount of gas embedded in the antibubble, (ii) the level of saturation of gas in the bulk liquid [2], (iii) the presence of dust particles (< 0.5 μ m) in the gas, and (iv) three-dimensional flow effects. By accounting for these various effects, the dependence of the antibubble radius on its lifetime is clarified together with the role of surface rheology. Results thus demonstrate that controlling the size and lifetime of antibubbles is achievable.



Figure 1: Time sequence of antibubble formation using our in-house antibubble generator

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Mechanism of Emulsion Formation in an Organic Solvent in the Presence of Hydrated lons

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A two-electrode cell comprising a liquid/liquid interface has been used to study the water clusters formation in the organic solvent phase following the tetraalkylammonium chloride (TAACI) transport from the aqueous phase. The partition of chloride ions is controlled by the interfacial potential difference induced by the distribution of a common TAA⁺ ions in both phases. The transfer of hydrated chloride ions is accompanied by the transfer of TAA⁺ ions which concentration at the aqueous side of the interface can be monitored by the open circuit potential (OCP) measurement. The amount of TAACI transported at a given potential to the organic phase exceeds amount of TAACI which could be dissolved. It results in the water clusters formation in the organic solvent phase. The presented mechanism of this process involves an additional water transport to the organic phase completing dissolved water consumed by the water clusters formation. At higher concentration of TAACI in the aqueous phase this process leads to the formation of emulsion in the organic phase.

The analysis of OCP transients lead to the following mechanism of the water clusters formation In the first step the TAACI is transported to the organic phase to fulfill the partition of chloride anions. In the next step the chloride ions dissolved in the organic phase form the water clusters utilizing the initial presence of water in the organic phase and water transported by chloride ions. The expended water in the organic phase is replenish by its diffusion from the aqueous phase to fulfill the equilibrium. At any distance from the interface the partition of TAACI between the organic phase and the water clusters must be fulfilled. It can be expected that the partition of TAACI will be influenced by the water cluster size.



distribution of TAA⁺ controls the potential difference

Figure 1: A cartoon depiction of the mechanism of water clusters formation at a water/organic solvent interface associated with the superfluos extraction of TAACI into the organic phase.

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Microfluidic Synthesis of Microparticles for Acoustic Metafluids

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The extraordinary properties of acoustic (random) metamaterials, such as negative refractive index, originate from low frequency resonances of sub-wavelength particles. While most of these functional materials are fabricated by mechanical engineering, soft matter techniques coupled with microfluidics open a new synthesis route for all-fluid acoustic metamaterials [1]. As a demonstration, we have achieved soft 3D ultrasonic metafluids with negative index composed of large amounts of calibrated soft porous micro-spheres (Figure 1), acting like strong Mie resonators [2].

The wide variety of physico-chemical processes offered by chemical engineering allows for the full-control of the mechanical/acoustical parameters (elasticities/celerities) of these resonant micro-particles: from very compressible particles, made of soft porous rubber or nanoporous silica to very dense particles such as metal particles or core-shell structures (Figure 1).

To illustrate the strength of our "soft" approach, we have shown that it is possible to achieve soft 3D ultrasonic metafluids with several negative band [2,3]. The Poisson coefficient, which parametrizes the ratio of transverse-to-longitudinal sound celerities in the particles, is shown to be a relevant mechanical parameter to anticipate whether or not the second negative band will emerge. Going a step further, we also pave the way toward Anderson sound localization [4] and demonstrate functional flat metasurfaces capable of sound focalization [5].



Figure 1: Microfluidic-synthetized particles having all a size \approx 100 µm and very different mechanical properties. (a) Fluorinated oil droplets with a moderate compressibility; (b-c) nanoporous silica and macroporous rubbers with a strong compressibility; (d) core-sell structure with a soft shell and a dense core; (e) metal particles with a very high density.

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Effects of nanoparticles localized at the interface on single droplet dynamics in shear flow

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During processing, polymer blends and emulsions are subjected to complex flow fields. The droplet deformation, retraction, breakup and coalescence in these flow fields determine the morphology of the material, and consequently also the final product properties. The morphology can be optimized by adding nanoparticles. Nanoparticles which are located at the interface stabilize and refine the morphology by suppressing coalescence. However, the fundamental mechanisms by which nanoparticles affect droplet deformation and breakup are poorly understood. Therefore, this research will elucidate the impact of interfacially localized nanoparticles on single droplet dynamics. To gain fundamental insight a model system of a polymer droplet of PDMS in a polymer matrix of PIB is used and the in-situ and time-resolved droplet dynamics is visualized in a counter-rotating shear cell in combination with optical microscopy. Two types of silica particles are used: spherical particles with a radius of 100 nm, and fumed silica particles with a primary radius of 8 nm. The latter form aggregates with a radius of approximately 100 nm. Both types of silica have a hydrophobic surface and localize at the interface. The effect of the spherical particles on the droplet dynamics is limited, whereas fumed particles considerably affect droplet dynamics. A high concentration of fumed silica particles reduces droplet deformation significantly, resulting in suspension-like behavior. When the Ca number surpasses a critical value, the particle network locally breaks up, resulting in localized deformability of the interface and breakup dynamics characterized by extremely irregular shapes. Finally, the destruction of the interfacial network results in hysteresis effects in the droplet deformation. These results suggest that an elastic particle network is formed at the droplet interface. Interfacial shear rheology and compression experiments qualitatively support this hypothesis as an elastic particle network is built up which can be broken down by shear.



Figure 1: a) Unusual droplet breakup of particlecovered droplets at $Ca_{eff} = 1.46$, b) Sheared droplets with wrinkled interface, c) Wrinkling of planar interface and fast fourier transform of the image.

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Sequential gelation of binary colloidal gel networks

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The assembly of binary colloidal mixtures into soft amorphous solids has gained increased attention due to their interesting physical properties and myriad potential applications. The aim of this research was to study the structure and mechanics of nonpolar gels arising from binary colloidal particles that exhibit intraspecies short-range attractions: fumed silica and triglyceride crystals. Gels were prepared by sequential gelation of tripalmitin crystals within a pre-existing silica network at varying relative concentration of the two colloidal species. Morphology and mechanical properties of the resulting gels were investigated by confocal microscopy and oscillatory shear rheology. Confocal imaging confirmed the existence of binary networks made up of needle-like and spherical-like triglyceride crystals aggregates depending on the relative concentration of the two colloidal species. Oscillatory rheology showed that gelation of the thermo-responsive tripalmitin crystal network within the pre-existing silica network improves the structural integrity of the gels. By varying the relative concentration of the colloidal species, the linear viscoelastic moduli and vielding behaviour of the gels were tuned from 'fragile' to 'robust', resulting often in gels with mechanical properties superior than their individual gel counterparts. Our results illustrate how sequential gelation of colloidal species with intraspecies interactions can influence the morphology and rheology of thermo-responsive colloidal gels.



Figure 1: Confocal image of a binary colloidal gel displaying silica aggregates ¢≈1% (orange), tripalmitin aggregates ¢≈5% (black) dispersed in oil (green)

Microrheology of DNA Hydrogels

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Using the binding specificity of DNA we study the emergence of viscoelasticity in hydrogels made of DNA building blocks as they are cooled below the melting temperature, T_m , of their 'sticky', single-stranded (ss)DNA overhangs [1-3]. Using Diffusing Wave Spectroscopy for micro-rheology, we have shown that a 1:1 mixture of Y-shaped DNAs with complementary sticky overhangs is in the fluid state well above the melting temperate of the overhangs, while undergoing a characteristic percolation transition at T_m and a fully formed 3D-hydrogel well below T_m [1-3]. The resulting overall elastic plateau in $G'(\omega)$, measured over many orders of magnitude in frequency, shows a dramatic increase when we remove the flexible joint between the Y-shapes which is provided by build-in, non-binding thymine (T) connectors. When going from a system of only Y-shapes to a mixture of Y-shapes and linear DNA linkers bridging them, we se an even more dramatic change in the network formation. In fact choosing the length of the fully flexible T-joint we can tune the system from a gel network to a system that remains liquid at al temperatures with lower viscosity than at high temperatures [4].



Figure 1: (*left*) Cartoon of the typical Y and Y' shaped DNA building blocks with sticky overhangs. (*middle*) Snapshot of a hydrogel formed by these Y-DNAs, obtained using a coarse-grained simulation model. (*right*) Photograph of such a hydrogel – containing 2 volume percent of DNA.

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Controlling microstructures in depletions gels: Effects of quenching rate, depth and shear flow history

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Depletion flocculated colloidal gels are versatile and industrially relevant systems, which help us understand the intricacies of structure development of such non-equilibrium systems. Pronounced changes in mechanical properties often result from subtle, highly localized microstructural rearrangements in a locally heterogeneous, disordered structure, which are difficult to resolve using ensemble averaged techniques as e.g. light or X-ray scattering [1], but require microscopy techniques [2]. In the present work, we evaluate the microstructural basis of the rheological properties, and in particular of the thixotropy and yielding in gelled colloidal suspensions by directly imaging colloidal gels during transient simple shear deformations and steady state flows. The experimental approach relies on the quantitative study of the gel microstructure using ultra-high-speed, structured illumination confocal microscopy.

Model systems of PMMA-g-PHSA [3], depletion flocculated by non-adsorbing polymers are used, and particular attention is given to controlling residual charges and how to screen those in a controlled manner by diffusion of an organic salt. This way, well controlled initial structures can be produced. Flow experiments are performed using a rheometer with a home-made shear cell for counter-rotation of the lower glass plate, allowing single particles to be imaged for long times at the stagnation plane. Fast axial scanning is implemented using an electric focus tunable lens, circumventing issues of immersion oil squeeze flow typical of mechanical focus repositioning. The unprecedented combination of temporal and 3D spatial resolution of our setup allows the study of intermediate volume fraction gels at high shear rates and with larger than usual fields of view, a critical factor to resolve the large length scales of structural heterogeneity developing in these systems. The results show that the anisotropic nature of a shear flow, combined with the subtle hydrodynamic interactions, first leads to an increased heterogeneity and anisotropy, which will be compared in detail with recent full hydrodynamic simulations [4]. The critical conditions for complete liquefaction of the structure will be identified and the structural recovery as a function of pre-shear history and interaction strength will be quantified.

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Rheology of surfactant-microgel mixtures: jamming and liquid reentrant transitions

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Stimuli-responsive microgels are colloidal particles made of crosslinked polymeric networks that undergo a volume transition in response to changes in pH, temperature, or solvent quality. Since particle swelling provokes a dramatic increase of the volume fraction, viscous solutions and randomly jammed suspensions with yield stress properties can be obtained at low polymer content. These features are exploited to design smart rheology modifiers used in cosmetics, pharmaceuticals, and food products.

In this communication, we explore a new strategy based on mixtures of microgels and ionic surfactants used as trigger. Using a combination of scattering (DLS, SAXS), fluorescence and interfacial techniques, we show that surfactants adsorb onto the polymeric network of the microgel thereby increasing its solubility. An additional important contribution to the swelling comes from the counter-ions which create an osmotic pressure that opposes that of the bath. At high surfactant concentrations, saturation occurs and the excess surfactant form free micelles outside the microgels. We thus expect significant changes in the rheological properties when both microgel and surfactant concentrations are varied.

The viscoelastic properties are investigated using oscillatory rheology. *At low polymer concentration*, the solutions have a purely viscous behavior at any surfactant content. As surfactant concentration increases, microgels swell provoking an increase of the low-shear viscosity. *At higher polymer concentration*, the particles first jam and form a soft glass with remarkable solid-like properties; at higher surfactant concentrations, a reentrant liquid transition is observed (see Figure 1). We demonstrate that this transition arises from the existence of attractive interactions driven by the osmotic pressure exerted by the free micelles^[1]. A phase diagram synthesizes the mixtures properties when the composition is varied. Our results open new routes to design yield stress fluids for a variety of applications by playing on the microgel architecture and the surfactant nature.



Figure 1: a) Evolution of low-shear viscosities with surfactant concentration for a fixed content of microgel. Cryo-TEM image of microgel-surfactant b) in the liquid phase c) with attractive interactions.

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Signatures of ageing in slow dynamics and rheology of dense hard and soft colloidal particles

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Concentrated colloidal systems where particles interact with short or long range repulsions often exhibit an interplay between equilibrium crystalline phases and long-lived metastable glassy states where the system is kinetically trapped due to entropic constrains in an amorphous state although thermodynamics would favor crystal formation. With the hard-sphere paradigm as a starting point we explore experimentally such interplay in a wider range of repulsive colloidal particles including soft core-shell microgels, polymer grafted particles and multiarm star-like micelles. More specifically we investigate the waiting time (ageing) dependence of the internal microscopic dynamics as probed by the appropriate multi-speckle dynamic light scattering (MSDLS) techniques as well as the macroscopic mechanical response measured by different linear and non-linear rheological tests.

While hard (or nearly hard) sphere colloids around the glass transition exhibit an ageing slow alpha relaxation process (related with out of cage diffusion) with clear intermittent character their elastic plateau modulus in the glassy state does not exhibit significant ageing. However nonlinear tests such as low stress creep and start-up shear experiments reveal both intermittent avalanche type events and waiting time dependent stress overshoots.

On the other hand in concentrated suspensions and glasses of soft colloidal particles the internal dynamics probed by MSDLS exhibit non-monotonic time dependence. Immediately after a rejuvenation (either thermal or mechanical) the alpha relaxation exhibits a slowing down, but after some long (and system dependent) waiting time a speed up is observed often linked to slow crystallization of the sample. Hence glassy states of soft colloidal particles, in contrast to their hard sphere counterparts, do age towards what seems to be an equilibrium crystal state. Rheological measurements as a function of waiting time in such systems reveal some common characteristics with the hard-sphere systems, but also interesting differences, such as the absence of intermittency in creep tests.

Rheology Transland and Philippe and Share and

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Using 3D real-space imaging, the translational and rotational motion of spherical and elliptical PMMA/PMMA core-shell colloids can be studied. To date, nearly all real space imaging experiments of colloidal particle dynamics have been focused on monitoring translational motion of spherical particles. While the rotational dynamics of spherical particles have been studied in detail on a single particle level ^[1,2,3], the dynamics of anisotropic particle received only little attention due to difficulties in synthesis and sufficient 3D imaging and analysis techniques^[4,5].



Figure 1: Scanning electron microscope image (A) and confocal microscope image of PMMA/PMMA coreshell ellipsoids. 3D representation of all ellipsoids detected within one image volume (C).

In this contribution, we present novel PMMA/PMMA core-shell ellipsoids with a spherical core and an elliptical shell labelled with different fluorescent dyes (figure 1 A and B), which are well suited for 3D confocal microscopy ^[6,7]. The detection of each ellipsoid within the 3D image volume requires new image processing tools. To this end, we developed an algorithm able to detect each ellipsoid in position on subpixel accuracy and orientation within accuracy of 5° as indicated in figure 1 C)^[7]. Using this approach, we experimentally study the structure and dynamics of a 3D system of monodisperse ellipsoids over a wide range of volume fractions. Our results provide insight into the phase behavior of ellipsoids in 3D and show both glass formation and nematic ordering ^[8].

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Electrodynamics of voltage-driven particle compaction investigated with total internal reflection measurements

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Electrophoretic displays exists for over a decade and have been successfully commercialized (ereader, electronic shelf label,...), but no video-speed applications have emerged so far. In this work we investigate the electro-optic dynamics of electronic inks with high pigment particle and high surfactant concentrations near the liquid-surface interface in devices optimized for videospeed applications^[1]. Experiments are carried out with a fluorochemical electrophoretic ink containing pigment particles inserted between to glass substrates separated by 25 micrometer spacers. The substrates are covered with an ITO electrode and a dielectric coating of poly(pxylylene) polymer Parylene C with a thickness of 50 or 200 nm. During a step voltage driving pattern we measure the transient currents and the total internal reflection from one surface using the reflection of a laser source under a skew angle through a prism. Transient current measurements show clear capacitive screening, resulting from the voltage drop over the dielectric Parylene C coatings. The total internal reflectivity measurement is visualized in Fig. 1. For a voltage step from -10 V to a higher voltage, visualized in Fig. 1 (a), we see a fast increase in reflectivity. For a step function from 10 V to a lower voltage, visualized in Fig. 1 (b), we see a two-stage switch from a high towards a lower reflectivity. The steady state reflection shows a high reflectivity for low voltages and an decreasing reflectivity for higher, with a characteristic transition at 3V. Based on an analytical model with positive pigment particles, negative inverse micelles, dielectric coatings and including positive, fixed surface charge on the dielectric coatings we can explain the observed steady state behavior. The full dynamic characteristics are reproduced with finite difference time domain simulations based on drift and diffusion.



Figure 1: Total internal reflection measurements during driving with a stepfunction from (a) -10 V to a higher voltage, (b) 10 V to a lower voltage

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Rheology optimization of ophthalmic eye drops formulations using a high shear microfluidic rheometer

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Topical application represents the main route of drug administration for eye disorders. It has been shown that the ophthalmic formulations efficiency is strongly related to the rheological behaviour, as blinking phenomena exerts high shear rates on eyedrops (up to $30,000 \text{ s}^{-1}$) [1]. Formulations must be carefully optimized to respect patient compliance and the adequate retention time. We present a new innovative method based on microfluidics, to measure viscosity as a function of shear rate (up to 10^5 s^{-1}) in a single experiment set-up. During the measurement, a sample and a viscosity standard (reference) are pushed together through a microfluidic chip (Y-junction) at controlled flow rates. Images of the resulting laminar co-flow are analyzed. The relation of the widths is proportional to the flow rate ratio and the viscosity ratio of reference and sample.



Figure 1: Measurement principle (left) and typical flow curves of eyedrops during high shear rate measurements.

In this work different formulations of eye drops were analyzed with Fluidicam^{RHEO} over shear rates ranging from 150 – 180 000 s⁻¹ at 34 °C (corneal surface temperature). Depending on the purpose, formulation of eye drops must be adapted. Newtonian formulations (purple, grey and yellow squares) are used for cleaning reasons with viscosity values around tears viscosities, providing a short retention time to clean the corneal surface. Non-Newtonian formulations (red, pink, green and blue dots) can reach high viscosities at low shear rates providing a higher retention time for therapeutic treatment and comfort at higher shear rate thanks to the shear thinning profile [1,2]

FLUIDICAM^{RHEO} allows accurate viscosity measurement at shear rates representative of the blinking stress, even for low viscous samples. With this information the formulation of eyedrops can be optimized to fulfil the application purpose (cleaning or therapeutic).

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Understanding viscosity changes in Polyelectrolyte Surfactant Complexes

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Mixtures of polyelectrolyte and surfactants (PESCs) are found in a wide range of industrial applications, from enhanced oil recovery operations to home and personal care products. While polyelectrolytes are mainly used for their unique rheological properties, surfactants are usually employed for their ability to adsorb and lower the energy of surfaces.

These mixtures are described by Z parameter (polyelectrolyte/surfactant charges) and they form a phase diagram in which solutions with excess of both polyelectrolyte (PE) and surfactant (respectively low and high values of Z) are clear and homogenous, while precipitates are formed around charge equilibrium.

In our work, we have investigated PESCs consisting of PE JR 400 (cationic, cellulose based polymer) and two different surfactants, namely sodium octyl sulphate (SOS) and sodium tetradecyl sulphate (STS). Because SOS and STS only differ in the length of their alkyl chains, it was possible to study the effect of the surfactant tail length on the rheological properties of the solutions. In a preliminary study, the system's phase behaviour and viscosity have been investigated, showing that the viscosity of JR 400/STS is significantly increased near the phase boundary, while JR 400/SOS does not show any viscosity changes. Near the phase-boundary, in PE-STS solutions SANS measurements showed the formation of an interconnected network of rod-like aggregates composed of a polyelectrolyte/surfactant complex, responsible for the viscosity increasing due to the high degree of interconnection between PE chains. For the PE-SOS solutions, instead, any compact rodlike aggregates are found, and the q⁻¹ slope in SANS curve is lost. These results found a good symmetry in Molecular Dynamics Simulations that we performed on these systems. In conclusion, because of a different microstructural organitazion of polyelectrolyte/surfactant complexes, the surfactant tail length is a crucial parameter in determining rheological properties of these mixtures.



Branched surfactants: An effective strategy for the design of high concentration/low viscosity surfactant formulations

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The rational design of branched-tail surfactants is a suitable strategy to obtain low-viscosity surfactant-rich isotropic aqueous mixtures with negligible effects on biodegradability. This opens a way to the design of concentrated ("water-free") surfactant formulations, highly attractive for their ecological and economic benefits.

The aggregation behaviour of N,N-dimethyl-2-propylheptan-1-amine oxide (C₁₀DAO-branched) in aqueous mixtures is investigated across the entire composition range by POM, SAXS, SANS, EPR, and PGSTE ¹H NMR. The humidity scanning QCM-D technique is validated as a tool for the fast screening of surfactants phase behaviour. Furthermore, the shear viscosities and viscoelastic moduli of the systems are determined by rheological measurements.

With respect to the linear isomer, C_{10} DAO-branched presents a much lower tendency to form lyotropic liquid crystalline (LLC) phases. Except for a narrow composition and temperature range in which a lamellar structure is observed, C_{10} DAO-branched aqueous mixtures are isotropic liquids whose microstructure changes, with increasing concentration, from micellar solutions to unstructured dispersions of hydrated surfactant molecules. Low-viscosity was found for all these mixtures, including the most concentrated ones. Thus, the introduction of a single short side-chain in the tail is demonstrated to be an effective approach to increase the active concentration in surfactant formulations.



Figure 1: Effects of the tail branching on the $C_{10}DAO$ phase diagrams and viscosity.

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Connecting the viscoelastic response of dense nano-sheet suspensions to their bending stiffness

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Micron-sized nano-sheets such as graphene platelets can be used to make conducting inks or as fillers in composites to enhance their mechanical properties. At high concentrations beyond rigidity percolation, nano-sheet suspensions become yield stress fluids with a finite storage modulus. In this regime the elastic response of nano-sheet suspensions appears to be universal. Few-layer graphene in NMP solvent ^[1] and aqueous graphene oxide dispersion^[2] exhibit a power law exponent close to 3 as a function of packing fraction.

We present a new analytical model that explains this behaviour and connects the response to the elastic properties of single nano-sheets and their size (Fig. 1). We infer the bending stiffness of single nano-sheets from our rheological data which agrees well with previous AFM experiments on single sheets and simulations.

This model opens up the possibility to infer elastic properties of different nano-sheets from rheological data of the suspension rather than performing AFM experiments on single nano-sheets. Furthermore, this model may explain the mechanical enhancement of nano-sheet composites where a similar exponent can be observed^[3] (Fig. 1).



Figure 1: The storage modulus plateau G'_0 (see inset) as a function of reduced volume fraction $\phi - \phi_c$ for a few layer graphene suspension and a graphene composite, where ϕ_c corresponds to percolation. The red line is our model prediction for a nano-sheet bending stiffness of 0.4eV.

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Controlling Shear Thickening in Colloidal Dispersions by Shaped, Non-Colloidal Particles & Surface Friction

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Background: Colloidal dispersions shear thicken and it is desirable to control the onset and extent of this rheology. While tailoring particle size, shape, surface interactions, and solvent properties can all be used to systematically vary shear thickening, it has been shown that confinement can also affect suspension rheology due to the enhanced hydrodynamic interactions (Swan & Brady, JFM 2011). Simulations have also shown that confinement can induce shear thickening (Bian et al. JNNFM 2014).

Aim: Quantitative control of shear thickening through adding shaped particles and modifying surface properties.

Methods: Here, we exploit these results to control reversible shear thickening in colloidal dispersions by inducing confinement within the suspension by adding non-colloidal particles. Shear thickening in colloidal dispersions can be dramatically altered by the addition of non-Colloidal spherical and cubic particles (Cwalina et al. JOR 2015, AIChE 2017).

Results: At low volume fractions, the addition of non-colloidal spherical particles to the colloidal dispersion leads to an increase in the steady shear viscosity as well as the dynamic moduli. At higher volume fractions of non-colloidal spheres, the shear thickening power law exponent increases with the addition of non-colloidal particles. At higher concentrations of added, cubic particles, deviations from this shifting procedure are apparent as depletion attractions and confinement of the underlying colloidal dispersion lead to larger increases in the viscosity at both low and high applied shear stresses. Further effects are induced by the greater confinement afforded by adding large plate-like clay particles even at very low concentrations. Finally, the jamming volume fraction is studied as a function of the effective particle friction coefficient.

Conclusion: The results of this study provide guidance for formulating suspensions through control of particle shape and mixture concentration. Examples of the use of this effect in technologies will be given.

Intrinsic viscosity, Brownian motion and fluctuating Brownian stresslets

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The interplay between colloidal particles and their suspending fluid is well known since Einstein's seminal work of 1905: the atomic composition of the fluid gives rise to the Brownian motion of the colloids, and the presence of colloids increases the viscosity of the suspension. Using theory or simulations based on analytic solutions of the flow field around a slowly moving spherical colloid, one may show that the intrinsic viscosity of this simple suspension amounts to [n] = 5/2under shear. Statistical mechanics provides a second route to the intrinsic viscosity, by applying the Green-Kubo formalism to the spontaneous stress fluctuations of a quiescent suspension. yielding for this simple suspension the surprising result $[\eta] = 0$. We discuss the origin of this hitherto unnoticed discrepancy, thereby revealing a deficiency in current stress calculations, and propose a solution. In brief, the well-known fluctuation-dissipation theorem relating the strengths of the hydrodynamic frictional forces and the stochastic Brownian forces experienced by a colloid needs to be extended to include hydrodynamic stresslets and fluctuating Brownian stresslets acting on a colloid (with cross-correlations between forces and stresses). With this revision, agreement is recovered between the two approaches to the intrinsic viscosity for a dilute suspension of spherical particles. We present Brownian Dynamics simulations of ellipsoidal particles, ranging from oblate to prolate, to show that agreement is also recovered for colloids of more complex shapes. The newly introduced stress term is found to alter both versions of the intrinsic viscosity in this case, with the intrinsic viscosity determined under shear being less affected.

Effect of Molecular Crowding on Conformation and Interactions of Single-Chain indexOberdisse, Julian—textbf Nanoparticles

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Single-chain nanoparticles (SCNPs) are soft disordered nano-objects synthesized by intramolecular bonding of linear polymer chains with a finite fraction of reactive groups allowing internal crosslinking of the molecule. They may be investigated as a mimick of, e.g., intrinsically disordered proteins, in particular with respect to the effect of the crowded cellular environment on macromolecular properties. Here the conformation of synthetic SCNPs in presence of linear polystyrene crowding molecules has been studied by small-angle neutron scattering under contrast-matching of the crowders^[1]. A model describing the scattering of aggregating polydisperse SCNPs (see Figure 1) has been developed, resulting in the determination of the potentially squeezed size of the individual SCNPs within aggregates, their local chain statistics, and the average aggregation number, as a function of crowding. Two different crowders - of low and high molecular weight, respectively - are shown to have a different effect: while long chains tend to impede their aggregation above their overlap concentration, short ones are found to mediate depletion interactions leading to aggregation. Self-imposed crowding within the aggregates has a similar impact on chain conformation independently of the crowding of the surrounding medium. Our results are compared to recent simulations and is hoped to contribute to the microscopic understanding of the phase behavior of soft intrinsically disordered nanoobjects, and in particular the effect of crowding on biomacromolecules.



Figure 1: Schematic representation of the aggregation process of two SCNPs of monomer numbers i₁ and i₂ described by the addition of their individual SCNP masses, and obeying the same local chain statistics.

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Self Assembly & Supramolecular Systems SELF3 Specific ion and isomer effects at the micellization process: The case of surface-active ionic liquids

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Recently, it was demonstrated, that even small changes in the structure of counterions, such as the position of the substituent on an aromatic ring, considerably influence the micellization process.^[1] However, this effect was studied in the presence of added salt only, which also considerably affect the self-aggregation processes.^[2] Due to the possible variations in the structure (chain length and counterions), surface active ionic liquids (SAILs) turned out as an excellent model system for investigation of micellization process in the last years.^{[3],[4]}

In this contribution first, the influence of counterions (Cl⁻, Br⁻, l⁻, acetate (OAc⁻), methanesulfonate (OMs⁻), toluenesulfonate, (OTs⁻), trifluoromethanesulfonate (OTf⁻), trifluoroacetate (TFA⁻) and 2-hydroxybenzoate (salicylate, Sal⁻)) on the micellization of 1-dodecyl-3-methylimidazolium cation, $[C_{12}mim]^+$, in water will be presented. As it is evident from Figure 1a, representing the enthalpograms obtained by isothermal titration calorimetry (ITC) for these systems in water at 298.15 K, the counterions affect the crucially critical micelle concentration and enthalpy of the process. Next, the influence of the different position of the -OH group on hydroxybenzoate anions (Figure 1b) on the micellization process of $[C_{12}mim]^+$ in aqueous solutions will be shown and finally, the micellization of the 1-dodecyl-(2,3 or 4)-methylpyridinium bromides (Figure 1c) in water will be discussed.

The thermodynamic study of the micellization process was carried out by ITC in a broad temperature range and experimental data were analysed by help of corresponding model.^[3,4] Obtained results will be discussed in terms of ion and isomer effect on the micellization process in water.



Figure 1. a) The entalpograms for $[C_{12}mim][X]$ systems where X stands for \blacksquare , Cl⁻; O, Br; \triangle , l⁻; \square , OAc⁻; \diamond , OMs⁻; \bigtriangledown , OTs⁻; \bullet , OTf⁻; \Leftrightarrow , TFA⁻, and \blacklozenge , Sal⁻ at 298.15 K. Solid lines represent the fits according to the model. b) the isomeric hydroxybenzoate anions; c) 1-dodecyl-(2,3 or 4)-methylpyridinium bromides.

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Soft Quasicrystals

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Quasicrystals have a unique aperiodic order, which leads to diffraction patterns of 8-, 10-, or 12fold rotational symmetry. They have been discovered in 1982 by Dan Shechtman. Since then they have been found in more than one hundred binary and ternary metal alloys. Beginning in 2004 there have been reports on quasicrystalline structures formed by soft materials such as dendrimers, polymers and surfactants. This indicates that there might be general principles that favor the formation of quasicrystals, and if this would be the case, quasicrystals could be rationally designed with characteristic length scales up to the submicron range for photonic applications.

We have discovered quasicrystalline phases with 8-, 12- and 18-fold rotational symmetry for polymer micelles and binary colloid mixtures in water and organic solvents. Their stability range and phase transitions into FCC, BCC, and Frank-Kasper phases as a function of polymer concentration, temperature and size can be well determined by X-ray, neutron and light diffraction. From our studies it emerges that a condition for the formation of soft quasicrystals is a soft interaction potential that facilitates the formation of polytetrahedral arrangements. Using MD-simulations we are able to map the stability regions of a variety of crystalline and quasicrystalline phases in terms of the micellar volume fraction, core/shell- and size ratio. The phase diagram for the first time links previous reports of quasicrystals in nanoparticles, polymers and metal alloys as well as MD-simulations to provide a fundamental understanding of the structure and stability of quasicrystals.

Thermophoresis in self-associating systems: probing poloxamer micellization by opto-thermal excitation

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Due to its exquisite sensitivity to interfacial properties, thermophoresis, *i.e.*, particle motion driven by thermal gradients, can provide novel, exclusive, and often surprising information on the structural properties of colloidal or macromolecular fluids and on particle/solvent interactions at the nanoscale. Here, by using an all-optical thermal excitation technique, thermal lensing, we show that thermophoresis can be profitably exploited to investigate the self-association of an amphiphilic block copolymer, poloxamer P407, which takes place above a concentrationdependent critical micellization temperature (cmt). In particular we show that, around and above the cmt, the direction of the poloxamer thermophoretic motion displays a remarkable double sign inversion, which is fully correlated with a peak in the thermal expansivity of the solution marking the progressive dehydration of the propylene oxide groups of P407 and their incorporation into the micellar core. In addition, the time-dependence of thermophoresis, when contrasted with the microscopic Brownian dynamics measured by dynamic light scattering, displays an unexpected slowing down within the region where the poloxamer self-association takes place. A semiquantitative understanding of this rather puzzling behaviour of the thermophoretic mobility and of the Soret coefficient in the P407 micellization region requires one to consider a model of thermophoresis for a system displaying a temperature-dependent equilibrium between coexisting species^[1]. Such a model suggests that other effective forces, besides those usually assumed to explain thermophoresis, are at work. Altogether, our results indicate that thermophoresis can be a unique tool to unravel subtle restructuring effects in soft matter systems.



Figure 1: Temperature dependence of the Soret coefficient for solutions of P407 at a w/w concentration of 1% (triangles), 5% (circles), and 10% (squares). The arrows mark the temperature values where micellization begins.

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Self-assembly of model amphiphilic peptides in non-aqueous solvents: changing driving forces, same structure?

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Within the homologous series of amphiphilic peptides A_nK , both A_8K and $A_{10}K$ self-assemble in water to form twisted-ribbon fibrils with lengths around 100 nm ^[1]. The structure of the fibrils can be described in terms of twisted β -sheets extending in the direction of the fibril, laminated to give a constant cross section of 4 nm by 8 nm. A simple model considering a free energy penalty due to stretching of hydrogen bonds within β -sheets arising from the twist of the ribbons ^[2], and the interfacial free energy of the hydrophobic β -sheets which would favor their lamination, was able to reasonably predict the finite width of the twisted ribbons ^[3].

In this study, we characterize the self-assembly behavior of these peptides in non-aqueous solutions as a way to probe the role of the hydrophobic interaction in fibril stabilization.

Both peptides in methanol and N,N-dimethylformamide were found to form fibrillar aggregates with the same β -sheet structure and similar cross-section sizes as in water. However, the gellike texture, the slow relaxation in DLS experiments, and a correlation peak in the SAXS pattern highlighted enhanced inter-fibrils interaction in the non-aqueous solvents, in the same concentration range (Figure 1). This could be ascribed to a higher effective volume of the aggregates due to enhanced fibril growth and length, as suggested by LS and cryo-TEM analysis. These effects can be discussed considering how the solvent properties affect the different energetic contributions (hydrophobic, electrostatic, H-bonding) of fibril formation. In the analyzed case the decreased H-bonding propensity of the non-aqueous solvents made the H-bond formation along the fibril a key driving force to the peptide assembly, whereas it represents a non-relevant contribution in water ^[4].



Figure 1: a) The A₁₀K samples in methanol (MeOH) and N,N-dimethylformamide (DMF) show gel-like texture. b) SAXS data highlight a correlation peak which is not seen in water.

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Multicharged organic bases as cross-linkers for polyelectrolyte complexes formation

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Polyelectrolyte complexes are used as flocculants, antibacterial coatings, and carriers in drug delivery systems. The complexes of polymers with surfactants, oppositely charged polyelectrolytes and inorganic ions are widely studied. However, complexes with low-molecular weight organic counterions are practically not represented in literature.

This work investigates the interaction between PAA and low-molecular weight oligovalent cations. The chosen polyelectrolyte is not only rather simple model compound, but also is nontoxic polymer, which have specific biological activity, can hide the bitter taste of drugs and, thus, a good candidate for using in drug delivery systems. As counterions two types of oligovalent amines were studied: 1) oligoethylenimines with various number of aminogroups and their naturally occurring analogies (spermidine, spermine); 2) di- and tetrafunctional amphiphilic substances, containing hydrophobic fragment based on aliphatic diols and natural aminoacids residues. Conditions of water-insoluble complexes formation were investigated by turbidimetric and potentiometric titration. The characteristics of obtained complexes were studied by DLS, NMR, FTIR, SEM, AFM.

lonic complexes of PAA with first type of counterions demonstrated reentrant behaviour. Complexes sensitive to different pH values were obtained by changing the number of NHgroups in the crosslinker. Upon interaction of polyanion with aminoacids derivatives, strong dependence of water-insoluble complex formation conditions on crosslinker hydrophobicity was observed. In both cases, we were able to obtain complexes in a form of film or nanoparticles with controllable size.

The results of this work relate to relatively poorly studied area of macromolecular chemistry interaction of polyelectrolytes with oligomeric organic counterions. Our results showed that such interaction could be useful method for design of macromolecular structures of different functional purposes, since pH-sensitive biocompatible products with different morphologies were obtained.

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Different scenarios on the equilibration of polycation – surfactant solutions at water/vapor interfaces

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The study of polyelectrolyte–oppositely charged surfactant solutions, both in bulk and close to interfaces (fluid and solid ones), has undergone a growing development in the last two decades, mainly due to its application in a broad range of technological and industrial fields, e.g. drug delivery systems, food science, tertiary oil recovery or cosmetic formulations for hair care and conditioning. Most of such applications take advantage of the chemical nature of the compounds involved, structural features of the formed complexes and the rich phase diagram of these systems.^[1,2] It is worth mentioning that the extensive research on this topic has risen a strong controversy related to the description of the physico-chemical behavior of these colloidal systems. This is in part because the self-assembly of polyelectrolytes and surfactants leads to the formation of non-equilibrium complexes, which impact significantly in the properties of the solutions and their adsorption to interfaces.^[3]

This communication discusses the assembly in solution of binary mixtures formed by a cationic polymer poly(diallyldimethylammonium chloride) (PDADMAC) and two anionic surfactants, sodium lauryl ether sulfate (SLES) and sodium N-lauroyl-N-methyltaurate (SLMT) and a neutral surfactant, capryl-polyglucoside (APG), and the adsorption of the formed complexes at the water/vapor interface. The results show that independently of the surfactant considered, the interaction of the polyelectrolyte and the oppositely charged surfactant leads to the formation of kinetically trapped aggregates in solution which present a high efficiency for surfactant binding. The appearance of such kinetically trapped aggregates lead to the solution to the onset in the phase separation region, even though the complexes remain undercharged along the whole range of explored concentrations. Despite the similarities of the bulk behavior, the equilibration of the interfacial layers formed upon adsorption of kinetically trapped aggregates at the water/vapor can proceed following different mechanisms as was evidenced by surface tension, equilibrium and dynamics, and interfacial dilational rheology measurements.

The nature of the surfactant and the possibility of the complexes to establish cohesion interaction through the surfactant tails leads to two different scenarios on the equilibration of interfacial layers: (i) layers in which aggregates remain intact upon adsorption, and (ii) layers of extended polyelectrolyte-surfactant complexes formed due to the dissociation and spreading of aggregates after their incorporation at the fluid interface. These results evidence the critical impact of the chemical nature of the surfactants in the interfacial properties. It is expected that this work may contribute to the understanding the complex bulk and interfacial interactions of this type of system to exploit its behavior in different technological applications.

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Segregation in Drying Binary Colloidal Droplets on Superamphiphobic Surface

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When a colloidal suspension droplet evaporates from a solid surface, it leaves a characteristic deposit in the contact region. ^[1, 2] These deposits are common and important for many applications in printing, coating, or washing. ^[3-5] By using superamphiphobic surfaces as a substrate, the contact area can be reduced so that evaporation is almost radially symmetric, leading to the formation of spherical supraparticles. ^[6-8] When fabricating supraparticles from bidisperse colloidal aqueous suspensions, we observed a segregation during the drying process, leading to a core-shell morphology. The outer region is predominantly occupied by the smaller colloids forming a close-packed, crystalline structure. Towards the center, the number of large colloids increases, which are packed amorphously. The extent of this stratification decreases with decreasing the evaporation rate. Complementary simulations indicate that evaporation leads to a local increase in density, which in turn exerts stronger inward forces on the larger colloids. Our findings are relevant for the fabrication of supraparticles for applications in the fields of chromatography, catalysis, drug delivery, photonics, and a better understanding of spray drying.



Figure 1: Colloidal droplet evaporation on superamphiphobic surface.

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Self-assembly of Saturn Particles in Two-Phase Systems

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The self-assembly of particles can lead to building blocks for new materials with novel properties.^[1] To guide the self-assembly, particles are functionalized with patches. We functionalize the caps of round particles with patches, separated by the belt, and call them Saturn particles.^[2] Most often, these particles preferably interact with each other with their patches.^[3]

The used Saturn particles are produced by masking the belt region of the particles by float-casting with a soluble polymer. The caps are released from the polymer by plasma etching with oxygen plasma and are covered with gold by sputter coating. After solving the polymer, the Saturn particles with gold caps (see Figure 1) can be harvested.

Saturn particles do not show any self-assembly when added to a one-phase system (neither in a hydrophilic nor hydrophobic solvent). When dispersed in the right mixture of hydrophilic and hydrophobic solvent, Saturn particles connect via the belt (see Figure 2a and 2b) and form branches and chains. Dependent on the mixture and energy input, huge networks are formed (see Figure 2c).



Figure 1: a) SEM image of a single Saturn particle. b) EDX spectral map of gold for a selected area of a single Saturn particle.



Figure 2: Via belt connected Saturn particles at oil-water-interfaces. a) Sketch b/c) Confocal fluorescence microscopic image. The caps of Saturn particles show a fluorescence signal.

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Self Assembly & Supramolecular Systems

SELF2-2 Self-assembly of micro- and nano- particles and their application for Particular Matter (PM) reduction in air

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It is of interest to apply nanoparticles for various applications, including for air purification. The health of the world's population, the ecosystem, and climate change are considerably affected by air pollution resulting in up to 7 million premature deaths per year[1]. The main culprit is particulate matter (PM), which once inhaled go deep in the lungs and/or bloodstream[2].

A novel method is proposed here for cleaning air from PM based on self-assembly of CaCO₃ micro- and nano- particle arrays. Evaporative spin-casting is a widely used process for fabricating thin coatings of a nonvolatile component on solid substrates[3], while drop coating method is also so useful to coat and activate a solid surface. The process of air cleaning is performed by exposing the self-assembled arrays to polluted air, followed by adsorption of PM onto the porous structure of CaCO₃ microparticle arrays. Stability of the system in the environment situation has been studied using AFM. The results have shown that selfassembled nano- and micro- CaCO₃ particles can adsorb PM from air both in environmental and laboratory conditions [4].

In conclusion, our research shows that the self-assembly method, driven by an easy to perform evaporation of a surrounding solution, is an inexpensive and accessible way of preparation of such structures. Recyclability and the possibility of an industrial scale production make these particles an ideal candidate for applications in cleaning the air. In this process, the PM adsorbed on self-assembled CaCO₃ particles can be extracted and reused, if necessary.



Figure 1. Schematic illustration of the study.

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Self Assembly & Supramolecular Systems SELF2-3 Self-Assembly and Dynamics of Anisotropic Magnetic Colloids Induced by an External Magnetic Fields External Magnetic Fields

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Anisotropic particles are known to exhibit a rich phase behaviour. In addition to the usual gas, liquid, crystal and glassy states found for spherical particles, anisotropic particles such as rods are known to exhibit additional liquid crystalline phases. Here we present the field induced self-assembly and dynamics of novel anisotropic colloidal particles whose shape resembles peanuts. Being made up of hematite cores and silica shells, these particles align in a direction perpendicular to the applied external magnetic field. Ultrasmall-angle x-ray scattering (USAXS) studies on their self-assembled structures in sedimented samples reveal the formation of a nematic like phase [fig. 1(a) & (b)]. The anisotropic dynamics of these particles was investigated using multispeckle ultrasmall-angle x-ray photon correlation spectroscopy (USA-XPCS). Our results indicate that along the direction of the magnetic field the relaxation follows a compressed exponential behavior [1] while in the perpendicular direction (also the direction of gravity) an advective term together with a purely diffusive one explains the observed behavior [2] [fig. 1(c) & (d)]. To the best of our knowledge, this is the first report on the dynamic of micron size anisotropic colloidal particles [3].



Fig1. (a) USAXS pattern of crystalline sediment of micron size magnetic core-shell peanuts shaped particles in the presence of a magnetic field representing a nematic like phase (b) Real space micrograph of the same confirming the nematic like order.

Intensity auto correlation functions (c) parallel and (d) perpendicular to the applied field at different q's as measured by USA-XPCS.

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Superparamagnetic colloid's droplets evaporation under field

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The evaporation of colloids droplets is a naturally abundant phenomenon, often used as a way to create deposits of self-assembled particles on a solid substrate [1, 2]. Recently, it has been shown that whiskey droplets do not present the wide-spread coffee-ring effect due to the presence of some tension-active agents combined with polymers adsorbing on the solid substrate [3, 4, 5]. Moreover, it has also been found that modifying the shape of the particles creates capillary interactions among those particles and that these interactions can suppress the coffee-ring effect [6, 7]. In our work [8, 9], we took advantage of magnetic interactions among superparamagnetic particles [10, 11], along with the concentration of specific tension-active ions, to control the deposit's pattern. We show in this presentation that the magnetic field can be used as a remote control for the deposit structures in the appropriate conditions.



Fig. 1 : Details of deposits obtained with different magnetic fields (0G and 22.5G) and various PBS concentration (6. 10⁻³ and 50. 10⁻³ initial volume fraction). Each picture has been numerically colourized according to the corresponding field condition. The bottom picture is a zoom on the squared area.

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2D colloids in rotating electric fields: Tunable interactions and particle-resolved studies of generic phenomena

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Tunable interactions in colloidal suspensions attract great interest because of their fundamental and practical significance. Self-assembly in suspensions of micro- and nanoparticles is a common phenomenon in nature, opening a way to create new materials for photonics and catalysis. Apart from practical interest, colloidal systems are of great importance for fundamental studies, since they mimic molecular behavior and can be used in particle-resolved studies of generic phenomena in condensed matter.

In this work, we present our results of theoretical and experimental studies of two-dimensional colloidal systems wherein attractive interparticle interactions are induced and controlled by external rotating electric fields^[1-2]. By placing two-dimensional colloidal systems in external electric field rapidly rotating in the plane of system, we can effectively induce interparticle attraction, which is long-range, tunable, and non-pair. Magnitude of the interaction is controlled by electric field and evolution of the system can be imaged using video-microscopy, that opens a way for detailed studies of such fundamental phenomena as self-assembly, condensation and evaporation, melting and crystallization, spinodal decomposition, dislocation dynamics, nucleation and coalescence, surface phenomena etc. In this presentation, we consider (i) novel experimental technology for particle-resolved studies of colloidal suspensions in rotating electric field^[1]; (ii) prospective experimental regimes; (iii) results of interaction analysis^[3]; (iv) a novel method for experimental data post-processing^[2]; (v) phase diagram of a monodisperse system in external fields^[4].

The results open fascinating prospects in studies of many-body systems with tunable interactions, and, therefore, will be of interest to wide range of scientists in soft matter, physical chemistry, chemical physics, photonics, and materials science.

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Magnetocapillary self-assemblies: floating crystals that swim and dance

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Magnetocapillary self-assemblies form when soft-ferromagnetic particles are deposited on a liquid surface under an induction field^[1,2]. They emerge from the competition of a magnetic dipolar interaction and the Cheerios effect, an attractive force due to the deformation of the meniscus^[3]. Under dynamic fields, these self-assembled structures swim along the interface^[4]. Due to their conceptual simplicity, they allow to verify and expand our general knowledge of microswimmers^[5]. Different arrangements of particles can be built with different goals in mind: from simple one-dimensional swimmers to complex bio-inspired structures; from fast, controllable swimmers to cargo transporters and fluid mixers.



Figure 1: A triangular assembly of 500µm particles is submitted to a precessing magnetic field. Dyes allow us to see the fluid motion due to both the rotation of the whole assembly and the individual rotations of the particles.

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Metachronal waves for magnetocapillary self-assemblies

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When tiny soft ferromagnetic particles are placed along a liquid interface submitted to a vertical magnetic field, the balance between capillary attraction and magnetic repulsion leads to the self-organisation of particles into well-defined patterns ^[1,2,3]. We demonstrate that precessing magnetic fields induce metachronal waves on the periphery of those assemblies, similar to the ones observed for ciliate organisms. These metachronal waves produce a net and controllable locomotion at low Reynolds number. This collective motion of the particles takes advantage of many-body interactions in order to develop specific functions along fluid interfaces. We present an extensive study about these systems.



Figure 1: Typical magnetocapillary self-assemblies. (Left) Picture of the interface where the 7-bead assembly floats, emphasizing the deformation of the liquid around each particle. The 6 small beads form a hexagonal ring around the larger one. (Right) Assembly of 19 beads of three different sizes. The diameter of the smallest beads is 400 μ m giving the scale of the pictures.

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Molecular Mechanisms in Hydrogen-Bonding Rich Non-Aqueous Solvents

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Self-Assembly of surface-active molecules, which has been well studied in aqueous and nonpolar systems, is not as well understood in hydrogen-bonding rich non-aqueous solvents, such as glycerol. Understanding the self-assembly mechanism in these hydrogen-bond rich solvents is important fundamentally and industrially, where molecular organisation, complexation, and assembly of amphiphilic functional additives play an important role. Further, product formulations make use of non-aqueous solvents due to their desirable physical properties, such as high boiling points, low toxicity, and solvency for organic molecules^[1,2].

This work aims to study self-assembly of amphiphiles in hydrogen-bonding rich nonaqueous solvents and to assess the validity of the models^[3-5] designed for bulk and interfacial aqueous self-assembly. The air-liquid interface was probed using surface tensiometry for sodium dodecyl sulfate (SDS) in a range of solvents. The critical micelle concentration (CMC) increased in the following trend: water (**8.1 mM**), glycerol (**11.7 mM**), and ethylene glycol (**> 300 mM**), suggesting that the solvophobic effect is strongest in water. Surprisingly, a gel-like mesophase was observed for SDS in glycerol (**2 wt %**) and ethylene glycol (**10 wt %**). Polarised optical microscopy (POM) (**Figure 1A**) showed the presence of large fibre-like aggregates with macroscopic dimensions, larger than that of an aqueous SDS micelle. Rheology of the SDS in glycerol phase (**Figure 1B**) showed an elastic-dominated material, with an elastic modulus in the order of 10⁴ Pa. Small-angle neutron scattering (SANS) of this phase (**Figure 1C**) showed a lamellar phase at room temperature, that reversibly transitioned into a micellar phase upon heating. Such unprecedented structural characterization facilitates a discussion of the effect of the role of the hydrogen-bonding properties of the solvents in mediating self-assembly.



Figure 1 (**A**) POM image of 4 wt % SDS in glycerol, taken at 40 x magnification, with a 530 nm first order waveplate. (**B**) Frequency sweep rheology data for 4 wt % SDS in glycerol, with phase angle (**green**), elastic (**G'**, **red**), and viscous (**G''**, **blue**) moduli. (**C**) SANS data for 4 wt % SDS in glycerol showing the reversible phase transition with temperature.

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Nanostructured Materials interacting with Synthetic and Natural Lipid Mesophases: Challenges and Opportunities

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In spite of the tremendous achievements in the design, synthesis and preparation of nanosystems for medicine, the implementation of nanomaterials into biomedical applications is still very limited. One of the main issues is a scarce knowledge of the interaction of nano-objects and biologically relevant interfaces, from complex biological fluids to biomembranes, which also bears considerable relevance in determining the toxicity of nanomaterials. In this contribution I will provide an overview of our results on the interaction of nanostructured materials with synthetic^[1] and natural biomembranes.^{[2],[3]} Our approach entails the understanding of mechanistic details gathered in model lipid mesophases^[4] either based on bilayered structures (liposomes, supported lipid bilayers and giant unilamellar vesicles) or cubic mesophases.^[5] Unravelling the nature of these interactions also provide the opportunity to design new physico-chemical methods to gather compositional, structural and dynamical information on real cell membranes.

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Rational Design of Supramolecular – Supracolloidal Hierarchical Architectures

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Rational design of supracolloidal structures is an opened challenge in bottom up nanomaterials preparation. With respect to its feasibility, a crucial role is up to the complete control over the interaction mechanisms involved among the colloidal building blocks, specially when particles with different sizes and shapes are considered and, hence, when anisotropy must be taken into account. This can be achieved successfully, exploiting the potential of bile salts derivatives (BSDs). These molecules are able to self-assemble in supramolecular building blocks, namely tubular structures, designed with a strict, native binding site individuation, available for the chosen specific interaction with a secundary particle. The duality of these building blocks, able to work either as linkers or as templating surfaces, in combination with spherical particles composed by different materials such as PS (polystyrene) or PNIPAAm (poly(N-isopropylacrylamide)), allows for hierarchical structures preparation with various intriguing features (Fig.1) [1]. The work here presented mainly by means of confocal laser scanning microscopy (CSLM), highlights different hierarchical architectures arising from the interaction between BSDs supramolecular tubules and polymeric spherical particles, with a particular focus on systems characterized by discrete regularity, forming regular tridimensional arrays. Tridimensional regular arrays of objects are fundamental forms of organization of the matter. Several characteristics can originate from such structures that are fundamental in nature and largely exploited in modern technologies.



Figure 1: sketch of two supramolecular - supracolloidal pathways for hierarchical structures preparation

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Numerical insights on the volume phase transition of ionic microgels

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Microgels are colloidal suspensions of mesoscopic particles constituted by a cross-linked polymer network. Particularly interesting, for both applied and fundamental research, are PNIPAM-based microgels (whose size and mass distribution can be tuned by temperature), and those containing weak electrolyte monomers such as PAAc (also sensitive to the pH).^[1] The electrostatic effect of acidic groups or charged molecules into the polymer backbone plays

The electrostatic effect of acidic groups or charged molecules into the polymer backbone plays a fundamental role in defining their behavior, which is not yet completely understood.



Figure: Equilibrium snapshots of a single microgel particle across the Volume Phase Transition.

We study microgels structural features across the Volume Phase Transition (VPT) by performing extensive numerical simulations at single-particle level, building on a newly proposed coarsegrained model of disordered gel network.^[2] We show that the presence of (i) an underlying disordered polymer network, (ii) explicit counterions and (iii) a rough surface at the outer corona shell are key ingredients to reproduce the main experimental features,^[3] such as the inhomogeneous structure observed in scattering experiments and the shift of the VPT toward higher temperature when increasing the bare charge of the network.

Our model also offers new microscopic insights on the VPT of ionic microgels. In particular, we find that the microgel-counterions complex is almost neutral in the swollen state, while the presence of a net charge develops at the VPT, when the competition among the short-range solvophobic attraction and the long-range electrostatic forces gives rise to the onset of inhomogeneous deswelling among the core and the surface, also observed in experiments. Our study is a step toward a better understanding of the underlying microscopic mechanisms generating these and other interesting phenomena.

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Controlling self-assembly with light

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Light responsive materials have gained significant attention in the last years due to their application in photothermal therapy, sensing or as molecular motors. Supramolecular particles of ionic dye molecules and oppositely charged macromolecules have recently been used to create a wide variety of different particle shapes.^[1]These assemblies can be controlled by the dye structure, pH, ionic strength but most interestingly by light.^[2]

Inspired by these findings we used a cationic azo dye $(AzoC_{10}N_2O_2^{2^+})$ and an anionic polyelectrolyte to create well-defined supramolecular structures and study these with small angle neutron-scattering (SANS). The forming structures can be fully disassembled by illumination with UV light (354 nm), which triggers the *trans* \rightarrow *cis* isomerization of the dye. Since the *trans* state is the thermodynamic stable form, *cis* \rightarrow *trans* isomerization takes place immediately afterwards. The energy barrier for this process (80 kJ/mol) can be overcome by two mechanisms: collisions with solvent molecules driven by thermal energy or illumination with light at wavelengths larger than 400 nm.

We used time-resolved SANS to follow the thermal $cis \rightarrow trans$ isomerization and the consequent structure formation. This allowed us to study the formation mechanism as well as size, shape and polydispersity of the assemblies. Moreover, we compared the final aggregates at different temperatures and the structure formed when light is used to trigger the $cis \rightarrow trans$ transition. This comparison revealed that the final size of the structures and the rate of $cis \rightarrow trans$ isomerization are strongly correlated. A larger rate of isomerization results in faster structure formation and smaller assemblies.

With the presented system, we can efficiently control the thermodynamics and kinetics of the structure formation in a self-assembling system and elucidate the influence on the resulting assemblies.



Figure 1: The graphs show SANS curves (D11, ILL), the solid lines are fit with the model of a polydisperse hard sphere and a generalized Gaussian chain (from left to right).

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Self-assembled Triton-X-family based micellar clusters for different applications

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Non-ionic surfactants have raised considerable interest for many purposes due to their unique physicochemical properties. Nevertheless, it is still challenging to create novel convenient self-assembled multifunctional materials with high solubilization and encapsulation capacities by preserving their advanced capabilities to protect loaded cargos without altering their characteristics. Here we present extended concept of micellar clusters (MCs) formation (Figure 1). The formation aspects, inner structure and the role of external factors have been extensively studied. MCs can be used to efficiently load hydrophobic fluorescent compounds, nanoparticles and toxic compounds compared to free surfactants. Triton-X-based MCs provide a unique feature of selective permeability to hydrophilic ligand-switching proteins such as recently discovered UnaG and albumin (BSA) demonstrating bright "turn-on" fluorescence signal. The proposed strategies allowed us to successfully encapsulate and visualize newly synthesized anticancer PTR-58-CLB-CAMP peptide drug and show the anticancer activity of the obtained composite.



Figure 1: MCs formation scheme, visualization, encapsulation peculiarities and anticancer activity.

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Alkyloligoglycerides – An interesting class of greener nonionic surfactants

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Usually nonionic surfactants, e.g. poly(ethylene glycol)monoalkyl ethers (CiEis), are employed for many applications and their aggregation behavior in water has been intensely investigated a long time ago^[1,2]. In this study we focus on a rather new class of nonionic surfactants, namely alkyloligoglycerides (CiGis), which are not based on oil chemistry such as CiEis, but their head group is based on glycerol, which derives from fat and thereby from a renewable resource. Therefore, these surfactants are very interesting and their self-assembly properties were studied by means of surface tension measurements, static and dynamic light scattering (SLS, DLS), small-angle neutron scattering (SANS) and electric birefringence (EBR). In these experiments we varied the chain length of the surfactant as well as the number of glycerol units in the head group. Interestingly, in aqueous media the glycerol surfactants often tend to form disk-like micelles^[3]. This tendency is explained by surface tension measurements, revealing rather small head group areas compared to conventional nonionic surfactants. Using neutron scattering it can be shown that also concentration has a marked influence on the aggregation behavior, i.e. at high surfactant concentrations the disk-like micelles start ordering in a stack-like configuration forming a guasi-liquid crystal. Additional electric birefringence experiments allowed to study the relaxation dynamics of the micelles, thereby giving further information regarding their effective size and interactions in solution. From our studies we conclude that alkyl glycerides are an interesting class of surfactants with a complex aggregation behavior in aqueous media governed by their molecular architecture and which depends only little on temperature, thereby being markedly different to conventional CiEi surfactants. Given their self-assembly and solubilisation properties they are suitable candidates for further applications.

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Microbial surfactants: understanding self-assembly to prepare soft materials

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Soft self-assembled materials (hydrogels, coacervates...) are applied in many fields, from thickeners, to drug encapsulation, wound healing, etc... In the field of wound healing, for instance, soft self-assembled materials are not intrusive and unpleasant, as often found when polymeric scaffolds^[1] are used. In this sense, molecular self-assembly is an interesting alternative, provided the biocompatibility of the selected compounds. Microbial glycolipid biosurfactants, obtained from the fermentation of renewable resources, are a new class of compounds, the interest of which is their biodegradability and low cytotoxicity. However, their self-assembly properties are still poorly known^[2,3] and their applications in the field of soft matter practically not existing.

This contribution discusses the self-assembly properties of selected microbial glycolipids and the recent development of soft materials like temperature- and pH-responsive hydrogels and coacervates. We show that microbial glycolipid biosurfactants can form self-assembled micelles, fibers and bilayers, the formation of which depends on pH and temperature. These sot materials can then be used alone to form hydrogels in water or in combination with polymers to form coacervates, the properties of which will in turn depend on pH and temperature. The self-assembly will be shown via SAXS and cryo-TEM experiments, while the gelling properties will be analyzed using time, temperature and pH-resolved rheology experiments.

This presentation provides a new insight in terms of understanding the complexity of the physico-chemical behaviour of microbial glycolipid biosurfactants but it also shows that understanding their properties allows their use in the preparation of soft materials.



Figure 1: Microbial surfactants are produced from yeasts and can be used to make soft materials

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Carbon Nanocoatings Derived from Self-Assembled Monolayers of Hexayne Amphiphiles

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Amphiphiles comprising a reactive, carbon-rich hexayne unit are versatile precursors for carbonbased nanomaterials with controlled morphology. The supramolecular self-assembly and subsequent UV-induced polymerization of such molecules have for example been employed to prepare carbon nanocapsules from colloidal dispersions^[1] and carbon nanosheets from monolayers at the air-water interface.^[2] Recently, we have developed a synthetic protocol to obtain hexayne amphiphiles where the polar head groups can be tailored to facilitate their bonding to a variety of solid surfaces.^[3] Here we demonstrate the use of such surfactants for surface modification. To this end, we investigated the self-assembly of hexayne amphiphiles with a phosphonic acid head group from the solution phase onto smooth alumina (AIOx) surfaces. A well-ordered self-assembled monolayer (SAM) could be formed under mild conditions, which, upon UV irradiation, was converted to a carbon nanocoating that was mechanically stable across several tens of micrometers. This concept shows its potential as a facile route towards low-cost and large-area fabrication of conformal carbon nanocoatings on technologically relevant substrates.



Figure 1: Schematic illustration showing the UV-induced conversion of a self-assembled monolayer (SAM) of the hexayne amphiphiles into a carbon nanocoating. The anchor group A can be tailored according to its binding affinity with the substrate surface.

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Structural evolution of quantum-dot endowed fluorescent lipid bilayers on polymer cushion via liposome fusion

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Supported lipid bilayers with embedded quantum dots (SLB-QDs) represent a promising platform in biotechnology, for instance for novel devices with features of flexible structures. Moreover, SLB-QDs are also relevant to tracking of the vesicle fusion on surface *via* fluorescence visualization of the QDs in the resulting bilayer patches. However, little is known about the influence of embedded hydrophobic QDs on the formation process of SLBs *via* vesicle fusion,

and how the presence of hydrophobic QDs influences the morphology and SLBs. structure of the Such an is important to their understanding bioanalytical applications and potential cytotoxicity. The main goal of presented study was to examine in detail the structural evolution of CdS QD containing SLBs. Synchrotron X-ray reflectivity^[1] and atomic force microscopy^[2] were applied to monitoring bilayer structural changes as a function of incubation time, after mixed POPC/POPE liposomes with hydrophobic 4.9 nm CdS QDs intercalated in the membrane ruptured on a PEI monolayer to form an SLB.^[3] The structural properties such as thickness, roughness and surface coverage were observed over a period of



Figure 1: XRR reflectivity curves of POPC/POPE SLBs with 4.9nm CdS QDs at 3h, 14h, and 24h incubation time (A) and corresponding SLD profiles with schematic of the structural evolution and QD rearrangement (B).

3-24 h. Our results show strong perturbation in the self-assembled structure of bilayer due to QD incorporation. Furthermore, it was observed that SLB-QDs became thicker with increasing incubation time due to rearrangement of QDs in the lipid bilayer, which we interpret as the QDs being expelled from the inner leaflet to the outer of the bilayer (Figure 1B). Our results will provide valuable information on the structure of QD-containing fluorescent SLBs, giving unprecedented mechanistic insights on the temporal evolution of such SLB-QDs, which could have potential implications for drug delivery, cell toxicity, and related aspects of NP-cell interactions.

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Colloids in confined liquid crystals: a plot twist in the lock-and-key mechanism

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Bottom-up assembly of colloidal particles can be employed to efficiently build hierarchically ordered structures, such as photonic crystals, self-healing materials or sensors. Even more interesting are reconfigurable structures, where particles configuration and/or order (and, with them, optical and mechanical properties) change under the effect of external inputs, e.g. temperature, magnetic or electrical fields, chemical composition. The ability to address the dynamics and localize single particles is crucial for these goals. Complex fluids such as liquid crystals are perfect tools to gain control on the motion of colloidal building blocks. For instance, when nematic liquid crystals (NLCs) are confined in a vessel with tailored boundaries, bend and splay distortions can be used to position particles^[1].

Here, we introduce a "twist in the plot" by imposing a twist distortion in confined liquid crystals. We study NLCs in a twisted cell and cholesteric LCs. This new configuration allows molding the director field and the energy landscape for a colloid in the three dimensions. Moreover, twist provides a high degree of manipulability, since it can be easily tuned and controlled in our sample. In both twisted nematic and cholesteric LCs, the twist introduces a new length scale, the pitch, which competes with the other sample parameters (particle diameter, vessel thickness, wavelength of boundaries undulations), enriching the possible configurations for particles-boundaries interactions.



Figure 1: Particles-boundaries attraction and repulsion mediated by π-twisted cholesteric liquid crystals.

Depending on the pitch-to-radius and pitch-to-thickness ratios, the interaction can be attractive or repulsive. By tuning the pitch, it is possible to selectively promote or inhibit particle trapping at the docking sites^[2]. This behavior can pave the way to a switchable adsorption of colloids mediated by external stimuli able to adjust the twist. A tool is this direction can be provided, for instance, by photosensitive monolayers where molecular alignment is controlled by polarized light.

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Nanostructured inks based on gold nanoparticles and polyelectrolytes

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Evaporating colloidal suspension leads to the formation of a variety of solid patterns, ranging from the concentric rings of a dried coffee drop to the uniform deposits of solid pigments left after paint drying. In the last decade, several groups have shown that evaporating suspensions of plasmonic nanoparticles is an efficient way toward the elaboration of nanostructured functional devices such as for instance gauge sensors,^[1] substrate for Surface-Enhanced Raman Spectroscopy (SERS)^[2] or diagnostic tools^[1]. In spite of these achievements, the final deposited nanostructures are rather big (~ μ m) compared to the size of the nanoparticles, restricted to a limited number of 2D patterns, and the interparticle distance is poorly controlled, hindering the developed a new method to self- assemble gold nanoparticles in bulk (3D) before deposition on model surfaces with controlled roughness and charge density. The nanostructuration relies on electrostatic interaction between negatively charged surfactants stabilizing the gold particles and ammonium functions of a polylysine-polyethyleneglycol copolymer designed on purpose.

This presentation will first present the different structures (SAXS and cryo-TEM) obtained in bulk by complexation between nanoparticles and polymers (polyelectrolytes or grafted polymers). Then, the 2D patterns obtained with dispersions of individual nanoparticles after droplet deposition and drying on model gold surface will be described as a function of nanoparticle concentration, surface/nanoparticle interaction force (-1.5 $\leq F_{DLVO}$ (nN) \leq +1.8) and the speed of droplet deposition (0 \leq v (m/s) \leq 10). Finally, the influence of nanoparticle self-assembly in bulk on 2D patterns will be discussed.



Figure 1: Deposition of nanostructured inks using the inkjet printing technique.

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Surface lattice resonances in self-assembled plasmonic gold nanoparticle arrays

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Plasmonic nanoparticles of gold or silver are known for supporting localized surface plasmon resonances (LSPRs) due to their interaction with electromagnetic waves. Encapsulating these metal nanoparticles into soft cross-linked hydrogel shells allows the large area preparation of periodic, non-close packed monolayers. Core/shell particles spontaneously self-assemble at an air/liquid interface where they form hexagonally ordered superstructures. The interparticle distance can be easily varied in a large range by adjusting shell size or swelling state of the hydrogel shells at the interface. The structures can be transferred on a glass substrate. Due to the periodicity of the array, LSPRs can couple to diffractive modes and thus support surface lattice resonances (SLRs). The coupling regime strongly depends on the distance between the metal cores ^[1]. Furthermore, SLRs can be enhanced by homogenizing the refractive index environment. To achieve this, monolayers on glass are embeddeded in a polymer-matrix that closely machtes the refractive index of the supporting glass substrate ^[2, 3].

In this contribution we focus on the correlation between the interparticle distance in gold nanoparticle arrays and the strength and wavelength position of SLRs, i.e. the strength of electromagnetic coupling. To do so, we used UV-vis extinction spectroscopy to analyze the optical response of the self-assembled monolayers. Absorbance spectra show a red-shift and decreasing intensity of the SLRs with increasing distance between particles (Fig. 1). Moreover, monolayers with large spacing possess a pronounced resonance peak at lower wavelength. This peak is related to a purely plasmonic contribution from the single-particle LSPR of the particles. Additionally, we used theoretical simulations to support the experimental data.



Figure 1: Left: Atomic force microscopy image of a representative ordered gold array. The inset shows a digital photograph of gold monolayer on a glass substrate. Middle: schematic view of core-shell particles with their nearest neighbor center-to-center distance d_{c-c} . Right: SLRs resonances of coated monolayers with varying d_{c-c} .

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Effect of surfactant head structures on hydrogels formed by surfactant-mediated gelation (SMG)

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Background: Low molecular weight gelators (LMGs) can easily form a gel through a simple dissolution and cooling process in a solvent. In such gels, the LMG molecules form self-assembled fibrillar networks (SAFiNs) which arrest the solvent. An example of an LMG is the organogelator 12-hydroxyoctadecanoic acid (12-HOA) which gels various organic solvents but not water. However, it is possible that hydrogels can be produced by dissolving 12-HOA in an aqueous surfactant micellar solution, which is referred as the surfactant-mediated gelation (SMG) The SMG allows "hydrogelation by organogelator" without any chemical treatment on the gelator molecule.

Aim: We aimed to study the effect of surfactant head group structures on the hydrogel formation and properties.

Methods: A clear transparent solution was obtained when 12-HOA was solubilized in an aqueous micellar solution of surfactants such as cetyltrimethylammonium bromide and chloride (CTAB and CTAC), cetylpyridinium chloride (CPyC) at 80°C, followed by a gradual cooling to a room temperature.

Results: A network of fibrous aggregates was observed in the gel by using an optical microscope and a transmission electron microscope (TEM). Small and wide angle X-ray scattering gives a Bragg peaks derived from the gel fibre structure. Dynamic viscoelasticity measurement showed elastic or gel property. The values of storage and loss moduli (*G*' and *G*'') in the CTAB system were higher than in the CTAC and CPyC systems. It was also found that the minimum gelation concentration in the CTAB system was lower than the other two systems. Those results indicated stronger gel network is formed in the CTAB system among cationic surfactant systems. We also studied in the anionic and nonionic surfactant systems.

Conclusion: We found the kind of counter ion of cationic surfactant has an influence on gel network formation through the SMG.



Figure 1: Surfactant mediated gelation (SMG)

Understanding the factors that promote the growth of giant wormlike micelles in mixed surfactant solutions

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The concentrated surfactant formulations used in personal-care and house-hold detergency most frequently contain entangled wormlike micelles or other giant mixed micellar aggregates [1]. Despite the enormous application of such formulations in everyday life, their preparation is based on empirical recipes. Quantitative theoretical prediction of the effect of mixing of surfactants with different headgroups and hydrocarbon chains on the micelle length and of the formulation viscosity is still missing. The ambitious goal of our project is to create a quantitative theory, which solves the above problem and allows one to predict the size of the wormlike micelles at given surfactant composition, temperature and electrolyte concentration. At each step, we aim to achieve agreement between theory and experiment. Following the natural principle "from the simplest to the most complex", we started our study from single-component [2] and binary mixed [3] wormlike micelles from *nonionic* surfactants – polyoxyethylene alkyl ethers, $C_m E_n$. The key quantity is the micelle growth parameter, which is also known as free energy of micelle scission, E_{sc} . The interactions in both micelle headgroup region and micelle hydrocarbon interior contribute to the value of E_{sc} . In agreement with the experiment, it was established that the mixing of chains with different lengths is always nonideal and synergistic (Fig. 1a), and promotes micelle growth [3]. Effect acting in the same direction is the enrichment of the endcaps with the surfactant of smaller packing parameter that is better accommodated in regions of higher mean surface curvature. The model accurately predicts the growth parameter $E_{\rm sc}$ (Fig. 1b), and the micelle mean mass aggregation number in mixed nonionic surfactant solutions without using any adjustable parameters. Such agreement is achieved for the first time and represents a breakthrough in the field. The developed approach can be extended to ionic and zwitterionic surfactants and their mixtures with nonionics.



Figure 1. (a) Non-zero chain interaction parameter corresponds to nonideal binary mixing. (b) The theoretical curves for E_{sc} are in excellent agreement with experimental data; no adjustable parameters!

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Association of block copolymer micelles induced by hydrophobic terminal groups of hydrophilic corona blocks

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It is well-known that ABA amphiphilic triblock copolymers, where A is the hydrophobic block and B is the hydrophilic block can form physical networks of block copolymer micelles interconnected by shared unimers in aqueous media. In this communication, we show that a similar type of hierarchical self-assembly can be formed also by amphiphilic or doublehydrophilic diblock copolymers that contain a hydrophobic terminal group. It was reported^[1,2] that poly(*N*-isopropyl acrylamide) (PNIPAm) with dodecyl terminal group attached by using S-1-dodecyl-S'-(α, α' -dimethyl- α'' -acetic acid)trithiocarbonate as a chain transfer agent undergoes micellization in aqueous solutions. Here we show that micelles with either a hydrophobic core^[3] (Fig. 1a,b) or a core formed by an interpolyelectrolyte complex (Fig. 1c,d) and a corona of dodecyl-terminated PNIPAm can form micellar aggregates or physical gels. The association behavior and structure of the aggregates is studied by a combination of scattering techniques (light scattering, SAXS) and transmission electron microscopy.



Fig. 1. Micelar aggregates of poly(N-butyl acrylate)-*b*-PNIPAm (a – TEM at 25°C, b – TEM at 40°C) and poly(acrylate)-*b*-PNIPAm/poly(trimethylammonium ethyl methacrylate)-b-PNIPAm complex (c – Cryo-TEM, d – SAXS showing a correlation peak corresponding to the core-core distance)

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Low-temperature Surface Forces Apparatus and Application

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Surface forces apparatus is a unique tool for bridging a gap between nano-materials and real macro-materials sciences. Various SFAs have been developed to obtain fundamental information about phenomena at the solid-liquid interfaces and for confined liquids between solid surfaces in addition to studying origins of interactions. However, temperature controlled SFA measurements have been limited though the temperature is an important variable.

We have developed a low-temperature surface force apparatus (SFA) using a thermoelectric Peltier module.¹ The twin-path surface forces apparatus, which determined the surface separation using modified two-beam interferometry was employed as the basic SFA.² The apparatus could be operated at a temperature of -22 °C in air, and -11.5 °C in solution. The local cooling allowed stable control of the temperature, while minimizing the influence of the thermal drift, and easy access to the sample under the operation.

In order to demonstrate the performance of the SFA, the electric double layer (EDL) repulsion between silica-silica and ice-silica surfaces was measured in water (for silicasilica) and in a 10% aqueous ethylene glycol. An exponentially decaying repulsion of the



Fig. 1 A schematic illustration of the experimental setup of the resonance shear measurement based on a low-temperature surface forces apparatus.

decay length, 11.2 ± 1.0 nm, was observed. The surface potential of the ice was calculated to be -35 mV by fitting the data with the EDL model.

This apparatus was used to study tribological behavior of soft materials on ice. Rubbers exhibiting different viscoelasticities were studied to obtain interfacial properties at various applied loads. Together with a high temperature device, we hope to extend the scope of the SFA measurement.

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"Superhydrophobic" forces: gas meniscus formation and shape

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Hydrophobic surfaces exhibit attractive interactions in aqueous solutions termed as hydrophobic forces. They have been attributed to a change in molecular structure of water close to such surfaces, in line with observations of nanometer ranged interactions. However, also very long range (tens to hundreds of nanometers) interactions were found between hydrophobic surfaces. They have been attributed to the formation of a gas meniscus between the surfaces. Such a meniscus can from either from preexisting nanobubbles or by cavitation. On superhydrophobic coatings, however, the range of such attractive interactions can exceed even 10 μ m. A possible explanation for these extremely long ranged forces could be the formation and growth of a large gas meniscus from air trapped inside of the superhydrophobic coating.

We used colloidal probe atomic force microscopy to measure forces between a superhydrophobic surface and a hydrophobic particle while simultaneously imaging the contact region with laser scanning confocal microscopy[1]. We find gas meniscus formation and increase in meniscus volume with increasing separation as gas is drawn from the pre-existing air layer underneath the interface between superhydrophobic coating and water. Evolution of meniscus shape during separation will depend on liquid surface tension, air layer thickness, and on local pinning of the three-phase contact line. Single pinning events at the micro/nanoscale rough interface could be resolved in our microscale experiments, which are too small to identify them in macroscopic wetting experiments such as contact angle hysteresis and roll-off angle measurements.

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Interactions between bacteria lipopolysaccharide membranes

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Background, Aim & Methods

Lipopolysaccharides (LPS) is a key structural component of the outer membrane of gram-negative bacteria. Many antibacterial agents (ABAs) exploit electrostatic and hydrophobic interactions to disturb the membrane integrity. It is thus important to understand such interactions on a fundamental level. Here, the adsorption of LPS (Ra mutants) on mica and the surface forces they mediate have been studied using a surface force

apparatus (SFA) [1]. The effects of temperature, divalent cations and the presence of a cationic antimicrobial peptide on adsorbed LPS surface layers have been investigated.

Results & Conclusion

Our results [2] show that LPS-Ra adsorbs weakly onto negatively charged mica in water. However, upon addition of calcium cations at near physiological concentration (2.5 mM) at room temperature, an LPS bilayer or multilayer on mica is observed, pointing to the pivotal role of divalent cations in mediating LPS surface adsorption and LPS layer integrity (Fig. 1). At temperatures above the LPS-Ra Krafft transition temperature (36 °C), bilayer fusion could be observed as indicated by 9-10 nm steps in the force-distance profiles, suggesting that a single bilayer is squeezed Furthermore, cationic surface-active out. oligoglycine (a synthetic peptide tetramer) is found to adsorb to the LPS bilayers, evident from the resulting bridging attraction, indicating the potential of the oligoglycine tetramer as a bacterial coagulant.



Fig.1 Calcium cations play a pivotal role in mediating bacterial liposaccharide (LPS) surface adsorption and layer structural integrity

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PNIPAM-coated Brushy Beads and How They Collapse: How Environment Affects Brownian Motion

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Responsive colloidal particles are proving their usefulness in the worlds of drug delivery, mineral floatation, and responsive crystals. Poly(N-isopropylacryamide) (PNIPAM) is a responsive material that is used to coat such colloidal particles. These particles interact with their surroundings through their brush layers. Thus, controlling these layers controls the system. However, it is unclear how PNIPAM brushes change upon collapse, making these systems difficult to control. Two primary collapse mechanisms are known for PNIPAM: critical temperature, and co-non-solvency. We have developed a novel optical method to probe these collapse mechanisms and their differences.

When a brush-coated colloidal particle is attached to a surface, its Brownian motion will be defined by the spring-like characteristics of the brush. Thus, we may use the Brownian motion as a probe. Using optical interference, we measure the displacement between the particle and the interface. The spectrum of the Brownian motion can be described by a damped harmonic oscillator. Upon collapse, that spectrum changes. This change is different depending on whether the collapse is due to temperature, or co-non-solvency. For the temperature collapse, the damping dominates the Brownian motion. In contrast, in co-non-solvency collapse, we find that the Brownian motion is more elastic than dissipative. This new method shows distinct responses for each of the two distinct collapse mechanisms.



Figure 1: On the left is the schematic of the set-up. We combine the interference technique to measure the Brownian motion with the APD (avalanche photodetector), and an optical microscope (images on the right). We measure only the reflected signal of the bead indicated by the arrows.

Adsorption of DNA/Polyelectrolyte Complexes at the Air/Water Interface

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The interactions of DNA with oppositely charged macromolecules attract great interest mainly due to the application of DNA/polyelectrolyte complexes (polyplexes) to the gene transfection into target cells. In spite of intensive studies, details of the mechanism of DNA compaction remain unresolved.Most of the authors consider the polyplex formation in the bulk phase. Meantime, it is well known that the layers of amphiphilic molecules at liquid surfaces can be considered as physical models of biological membranes, and therefore the information on DNA/polyelectrolyte interactions in the surface layer can facilitate the understanding of the structure and formation mechanism of aggregates of these substances in biological systems.

This work is devoted to the investigation of surface properties of mixed solutions of DNA and hydrophobically modified polyelectrolytes - polymethylalkyldiallylammonium chlorides, and to the estimation of the adsorption layer structure. Other aims consist in the evaluation of the difference between polyplexes formed in the bulk phase and at the liquid – gas interface, and in the comparison with the surface properties of DNA/surfactant solutions^[1]. Measurements of the kinetic dependencies of the surface properties (surface tension, dynamic surface elasticity, ellipsometric angles) of DNA/polymethylbutyldiallylammonium solutions of chloride and DNA/polymethylhexyldiallylammonium chloride discovered a noticeable synergistic effect. The deviations from the results for solutions of individual components indicated the adsorption of complexes and the formation of a rigid network at the interface. The atomic force microscopy allowed estimation of the morphology of the adsorption layers as a function of the molar ratio of the two components and of their total concentration.

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Direct Force Measurements in Alcohol Solutions

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In recent years extensive experimental data on the interactions between colloids across aqueous solutions was collected. On the other hand, the information about particle interactions in non-aqueous solutions is still relatively scarce. For example, only a handful of studies measuring forces in alcohols exist, although such interactions are important in practical applications of colloids [1,2]. Furthermore, comparing interactions in non-aqueous media with the interactions across water is important also from fundamental point of view [3]. Here we present direct force measurements between silica particles in alcohol solutions. We study the influence of concentration of salt and type of ion on the force between the particles. We extend the force measurements with electrokinetic and colloidal stability experiments, which give us additional insight into the alcohol systems. In pure alcohol the interactions between silica surfaces is repulsive due to overlap of the double-layers. At high salt concentrations the interactions are attractive and the van der Waals force is dominant. Interestingly, the range of double-layer interactions in alcohols is longer as one would expect from the Debye lengths calculated from the nominal salt concentrations. This mismatch is due to pronounced ion-paring in alcohol solutions. In the presence of multivalent ions the charge neutralization and charge reversal of silica are observed. Charge reversal in alcohols is much stronger and shifted to lower concentrations as compared to the agueous systems.



Figure 1: (a) Scheme of colloidal probe experiment in isopropanol. (b) Forces between silica particles in isopropanol with added tetrabutylamonium bromide.

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The interaction between ions and adsorbed dipoles: why do we need quadrupoles in the Poisson-Boltzmann equation

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The macroscopic Poisson-Boltzmann equation is one of the fundaments of the colloid & interface science. One of its many limitations is that it neglects the quadrupole moment of the molecules of which the medium is formed. The quadrupolar Coulomb-Ampère law corrects this defect:

$$\nabla^2 \phi - L_0^2 \nabla^4 \phi = -\rho / \varepsilon \,,$$

where ϕ is the electrostatic potential, ρ – charge density, ε – dielectric permittivity (a measure of the solvent's dipole strength), and L_Q is the so-called quadrupolar length, a measure of the solvent's quadrupolar strength. This equation is of the 4th order and, in addition to Gauss's equation, has another boundary condition at every surface, according to which the bulk density of quadrupole moment (the quadrupolarization tensor **Q**) is conjugated with the surface normal dipole moment P^S as $Q_{nn}/2 = P^S$. Within this formulation of the macroscopic electrostatics, the intrinsic dipole moment of a surface (responsible for the measurable Volta potential) produces a strong field of range 0.5-1 nm from the surface of discontinuity.



Figure 1, left: the dipole moment of neat water surface is with the positive pole towards the aqueous phase, resulting in adsorption of anions. Right: an alcohol monolayer produces the opposite surface dipole and attracts cations.

We discuss several consequences of the electric field of the adsorbed dipoles:

- it orientates the polar molecules near the surface, producing a structure called the *dipole double layer* (consisting of adsorbed dipole layer and oppositely orientated diffuse dipole).
- It attracts ions. We show that neat water surface attracts anions, while surface with adsorbed alcohols adsorbs cations due to their dipole moment (see the figure).
- It seems to contribute to the Jones-Ray effect.
- The quadrupolar electrostatics allows to relate the empirical "surface dielectric constant" to the bulk values of ε and L_Q , and to predict to an extend the ion-specific effects on the surface dipolar & Volta potentials.
- It modifies the Gouy equation, and the electrostatic surface forces in a thin film.

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Surface forces-induced alteration of local dielectric properties in thin liquid films

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In this work, basing on the coupled dipoles method (CDM) with accounting for many-body interactions we have developed the approach for calculation of microscopic electric susceptibility and the local dielectric permittivity in thin liquid films. This approach allowed us to analyze how the van der Waals surface forces affect local dielectric properties in thin liquid films. It was shown that dispersion interaction between the molecules, even for the case of nonpolar liquid with weak intermolecular interactions, causes a notable variation in dielectric properties (see Figure 1) of thin film, which is manifested in the boundary layer formation.



Figure 1: Lateral and normal to film surfaces values of local dielectric permittivity across the free hexane films with different thicknesses (h2, h7, and h13 correspond to films with thickness of 2, 7, and 13 monolayers, respectively).

The Molecular Structure of the Interface between Organic Solvents and Hydrophobic Solid Surfaces

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An efficient stabilization is essential for the preparation of small organic nanoparticles^[1-2]. The stabilization mechanism of organic nanoparticles prepared by liquid antisolvent precipitation (LAS) in aqueous dispersion without additional stabilizers is under discussion. It is assumed that the solvent used during the LAS process contributes to a stabilizing layer at the interface of the nanoparticles.

As a well defined planar model system for a hydrophobic organic solid interface, we studied silicon wafers functionalized with octadecyl trichlorosilane (OTS). Using a specialized sample cell, the study of the interface structure formed between the solid and mixtures of an organic solvent and water could be performed by X-ray reflectometry (XRR) under equilibrium.



Figure 1: Sketch and electron density profile of an OTS coated silicon wafer in contact with an ethanolwater mixture. At the solid-liquid interface an organic solvent layer is forming.

A comprehensive analysis using a structural model which could consistently be applied to all measurements demonstrated the existence of an organic solvent layer which is in good agreement with MD simulations^[3]. The molecular arrangement and the concentration of the organic solvent within the layer is systematically correlated to the total solvent concentration of the solvent-water mixture and the polarity of the solvent used. Latter was classified by the Hansen solubility parameters.

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Omniphobic Slippery Titanium Surfaces as a Non-Toxic Alternative to Biocidal Anti-Biofouling Coatings

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The undesirable accumulation of biological matter on surfaces is a serious problem affecting a wide range of industries of our society. Biofilms in pipelines and heat exchangers provoke biocorrosion leading to equipment failure, biomedical devices, and food facilities suffer from an accumulation of harmful bacteria triggering the spread of infectious diseases and even human mortality, fouling of marine species in the shipping industry increases fuel consumption causing unnecessary CO₂/SO₂ emissions. Biofilms are often treated with antibiotics; but, the development of multiple drug resistance and adverse side effects are major drawbacks for conventional antimicrobial agents. Thus, novel approaches are required to prevent biofouling such as inspired by nature omniphobic slippery liquid-infused porous surfaces, which effectively repel various liquids and microorganisms.^[1,2]

Titanium (Ti) and its alloys are the natural choice for metallic material due to their low specific gravity, high mechanical strength, and resistance to wear and corrosion.^[3] In recent years, titanium alloys have been widely studied for medical applications due to their biocompatibility and non-magnetic characteristics and for naval purposes in which corrosion. erosion, and maintenance are of primary concern. Here we show a novel and universal approach of direct modification of the titanium surface characteristics by facile electrochemical anodization method to form a thin layer of micro/nano-porous titanium oxide. Upon modification with low-surface-energy compounds, these surfaces demonstrate superior droplet mobility with a contact angle of 180° and 0° contact angle hysteresis with excellent mechanical durability representing an ideal surface in the Cassie-Baxter superhydrophobic wetting state. Once infused with fluorinated lubricant, these substrates show exceptional resistance to bacterial and fungal attachment (Staphylococcus aureus and Candida albicans) and successfully resist most of the aquatic micro- and macro foulers such as mussel Geukensia demissa, barnacle Amphibalanus Amphitrite, marine bacterium Cellulophaga lytica and green algae Chlamydomonas reinhardtii without being toxic to the seawater environment.

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Assembly of surfactant-decorated nanoparticles at the air/water interface under external stimuli

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The assembly of nanoparticles (NPs) into monolayers at liquid interfaces has been at the focus of intense experimental and theoretical research in view of the potential enhancement of the magnetic, electric and optical properties of NPs monolayers [1]. However, a full comprehension of the interfacial inter-particle interactions driving the assembly upon NP adsorption at liquid interfaces is still missing, despite its critical role for the fine tailoring of the monolayer structure and properties.

The present work proposes a new approach to investigate these interactions by characterizing the structure of NP monolayers while compressing them in a Langmuir trough. In particular, we employed silica NPs, with a diameter of 19 nm and negatively charged, which, mixed with cetyl trimethylammonium bromide (CTAB), are able to form homogeneous monolayers characterized by a well-defined inter-particle distance depending on the NP/CTAB ratio [2]. After a systematic structural characterization of NP monolayers as a function of the CTAB concentration, carried out via synchrotron radiation grazing incidence small angle x-ray scattering (GISAXS), we show, by compressing NP monolayers in a Langmuir trough (Figure 1), that both the starting and the collapse inter-particle distances are significantly influenced by CTAB concentration, suggesting that adsorbed surfactant molecules play a key role in the mediation of the overall inter-particle interactions. Finally, from the surface work measured during the compression in the Langmuir trough and the inter-particle distance variation determined by GISAXS, we were able to obtain quantitative information on the order of magnitude of interfacial inter-particle repulsions in our case, being in the range of 10² pN, as well as on their dependence from inter-particle distance.



Figure 1: Surface pressure vs Area compression isotherm of 0.1% wt silica NPs at different CTAB bulk concentration (A), the corresponding monolayer collapse is indicated by arrows. During compression, interparticle distance determined by GISAXS progressively decreases (B) up to the monolayer collapse, after which inter-particle distance is constant.

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Interactions between *stratum corneum* lipids and fibre-additives: From interfacial structure to sensation of touch.

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Soft sensation of touch is often a key consumer satisfaction criterion, particularly in personal care products due to their intimate contact with sensitive anatomical parts of the human body (e.g. in nappies). Synthetic fibres in these products, when in a raw state, often exhibit rough, tacky surfaces of high coefficient of friction which can affect not only their processing (e.g. fibre breakage and production inconsistency) but also the final product properties (e.g. softness, strength and general appearance). Since human tactile discrimination extends to a few nm¹. characterisation of fibre surface nanostructure and nanomechanical properties is of high relevance. Here, we present nanoscopic characterisation of synthetic fibres (polyethylene (PE), polyethylene terephthalate (PET) and polypropylene (PP)) currently used in personal care products. Correlation between fibres topography gained with scanning electron microscopy (SEM) and atomic force microscopy quantitative nanomechanical property mapping (AFM QNM) showed that both the fibre manufacturing process and the surfactant treatment affect their morphology and nanomechanical properties. On polypropylene (PP) fibre surface treated with erucamide (13-cis-docosenamide; a common slip additive used in polyolefin film processing²). we observed overlapping multilayers of 4 nm erucamide bilayers, attributed to the slip additive migration onto fibre surface. Erucamide presence affected fibre adhesive properties, indicating its potential to provide lubrication. In order to establish an au fait structure-interaction correlation between the fibre coating and human stratum corneum (SC), we performed X-ray reflectivity (XRR) study on the erucamide layers and ceramide/cholesterol/fatty acid layers - the major constituents of lamellar sheet present in SC³. The structural information obtained with XRR study (layer thickness, density, molecular orientation, and coverage) underpins our fundamental understanding of the sensation of touch facilitated by the surface interactions they mediate, with implications to how tactile qualities such as softness can be enhanced and tuned with the presence of slip additives in fibre coatings.



Figure 1: (a) Schematic showing lipid interactions mediating touching sensation; (b) AFM QNM Height image for a PP fibre treated with erucamide; and (c) XRR curves of erucamide multilayers on silica at RT.

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What Makes SLIPS Slippery? Measuring effective slip on lubricated surfaces with colloidal probe AFM

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Slippery Liquid-Infused Porous Surfaces (SLIPS), inspired by the pitcher plant, possess selfcleaning and anti-fouling properties, with the potential for drag reduction.^[1-2] They achieve these properties by using micro- and nano-scale topography to trap a chemically compatible lubricant, creating a customizable liquid interface.^[3-4] Understanding the nanoscale forces that stabilise the thin lubricant film, and the ability of these films to reduce drag is crucial for their practical use under shear.^[5] Recently it has been shown that smooth surfaces are capable of retaining a lubricant layer, and the mechanism for this lubricant retention is unclear.^[6] Using colloidal probe atomic force microscopy, the flow of simple viscous liquids was studied over smooth lubricated surfaces, with the aim to quantify effective interfacial slip. The minimum lubricant film thickness that has slippery properties was quantified and related to macroscopic measurements of roll-off angles of water droplets over a partially dewetted lubricant film.^[7] Further studies have been performed on the drag reducing properties of stable lubricant films with thicknesses up to 800 nm.^[8] This work provides insight regarding liquid flow in confined geometries and on effective ways to minimise hydrodynamic drag.



Figure 1: (a) Scanning election micrograph of a colloidal probe used in hydrodynamic force measurements, with diameter of approx. 17 μ m. (b) Schematic illustration of the no-slip boundary condition on the left hand side, and partial slip boundary condition with corresponding slip length *b* on the right hand side. (c) Hydrodynamic force measured by colloidal probe AFM, where the experimental approach force curve is fitted with slip theory and an effective slip length *b*.

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Rheo-MAGIK: Combined neutron reflectivity with a novel interfacial rheometer to study interfacial structure-property relationships

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Interfacial structure and rheological properties are critically important in biological and many synthetic systems. Mixed flow fields tend to convolute the data interpretation of dilatational rheology at the interface in the presence of interfacial systems with both finite surface shear and dilatational elasticity. Attempts have been made to resolve the anisotropic state of stress into their pure forms, but few methods have succeeded in the Langmuir trough. One proposed method resolved the surface shear and dilatational elasticity through different Wilhelmy plate orientations relative to the moving barriers of the Langmuir trough, but sometimes these anisotropic states are not as easily decoupled.^[1] Pepicelli et al. rid the trough complexities of uniaxial compression by proposing a trough with radial symmetry.^[2] The radial trough was successful in determining pure surface dilatational elasticity through isotropic compression, but the interfacial morphology remained elusive with solely rheological analysis. A modified trough inspired by the radial trough called the Quadrotrough was created with shear and dilatational capabilities as a new sample environment for neutron reflectivity, or rheo-MAGIK, to understand the structural behaviour of air-liquid and liquid-liquid interfaces under homogenous interfacial deformation. Our hypothesis is that anisotropic compression will only affect the dilatational rheology for interfaces with finite surface shear moduli, which cause convolution of mixed flow fields and complicate data interpretation. On the other hand, interfaces with negligible surface shear moduli should show isotherms that are path-independent, meaning both isotropic and anisotropic compressions display identical isotherms. The design of this trough will be discussed and proof-of-concept model systems are used to evaluate the extent mixed deformations of shear and dilation can affect the isotherms created. Surface pressure isotherms are also investigated based on their path dependence of pure dilation and shear. Samples investigated include model steric acid monolayers as well as more complex macromolecules and monoclonal antibodies.

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Marangoni induced flow can lead to instability during drop merging

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The coalescence and interaction between two drops have been the subject of intensive studies in recent years [1], due to its wide range of application and the presence in the nature.

In this study two different liquids with different surface activities are studied. To study these phenomena, we deposit drops of different liquids on a substrate. The key point is that the merging process generates an instability (Fig. 1) if the liquid with higher surface tension is deposited first.

This instability is responsible for breakup of secondary drops on the first deposited drop. We present a detailed study of this instability analyzing the onset of the instability and characteristic length scales of the instability as a function of the physical parameters like the vapor pressure of one of drops. Finally a model is presented to explain the Marangoni induced flow by the gas phase. This model is validated by particle tracking.



Fig. 1: A cyclohexyl bromide drop (right) in contact to a water drop (left). This spreading film becomes unstable and disintegrates into small drops.

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STABILITY OF BUBBLES AT THE SURFACE OF A SOAPY BATH

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The stability of soap films has raised a lot of interest for both fundamental and industrial purposes in the last decades. The study of surface bubbles is generally motivated by their faculty to enhance material exchanges between the bulk and the overlaying atmosphere through the production of aerosols. This can be applied for example in climate models (production of sea-spray aerosols), air pollution studies in the vicinity of pathogen-bearing pools or in the carbonated beverage industry since the produced aerosols are enriched with surface-active materials that contain most of the flavour.

The quantity of produced aerosols depends on the shape of the bubble (its size for a given physico-chemical system) and on the thickness of the film upon bursting. This work will more specifically address the question of the bubbles size and the role of humidity in the evolution of the system before its bursting.

We present an experiment that allows to measure the lifetime of thousands of bubbles, which is necessary to characterize this system that features a stochastic contribution, in a humidity-controlled environment. We show that the bubble lifetime increases with the bubble size and the relative humidity. These results are completed by measurements of the thinning rate of the film at the apex of the bubble performed in the same conditions. We derive a model for the overall thinning of the film and a prediction for the lifetime of the bubbles that describes very well the collected data. Evaporation and more specifically the convective plume induced by the surrounding bath [1], are shown to play a major role in the lifetime of the bubbles.



Figure 1: surface bubble seen from the side. Marginal regeneration plumes are rising to the apex and contribute to the thinning of the spherical cap [2]

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The Chaotropic Effect as an Assembly Motif in Chemistry

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Following up on scattered reports on interactions of conventional chaotropic ions (e.g., I⁻, SCN⁻, CIO4⁻) with macrocyclic host molecules, biomolecules, and hydrophobic neutral surfaces in aqueous solution, the chaotropic effect has recently emerged as a generic driving force for supramolecular assembly, orthogonal to the hydrophobic effect. The chaotropic effect becomes most effective for very large ions that extend beyond the classical Hofmeister scale, and that can be referred to as superchaotropic ions (e.g., borate clusters and polyoxometalates). In this contribution,^[1] we present a continuous scale of water-solute interactions (Figure 1) which includes the solvation of kosmotropic, chaotropic, and hydrophobic solutes, as well as the creation of void space (cavitation). Recent examples for the soft-matter association of chaotropic anions to hydrophobic synthetic and biological binding sites, lipid bilayers, colloids, and surfaces are discussed.



Figure 1: Extended Hofmeister scale with specification of the superchaotropic, hydrophobic ionic, and superhydrophobic regions.

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Anionic Boron Cluster Compounds as Amphiphiles without Head-and-Tail Design

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Boron is one of the few elements that form large molecules through a series of covalent bonds. It yields borohydrides – boron cluster compounds, such as boranes, carboranes and metallacarboranes. The shape of boron clusters is atypical due to their electronic structure. Besides 3D σ -aromaticity, they are characterized by negative partial charge of hydrogen atoms that has important consequences for their bonding and solution behavior.



Figure 1: The electrostatic potential of [cobalt bis(1,2-dicarbollide)] anion.^[1]

During the last decade, we extensively studied solution behavior of cobalt bis(dicarbollide) anion, COSAN, its derivatives and other anionic boron cluster compounds such as decaborate and dodecaborate dianions.^[1-4] The primary question stands what is a driving force of their self-assembly in water. Another important aspect is their interaction with solvent, cosolutes and macromolecules, and their distribution in micro-phases. To answer our questions, we employed scattering, liquid&ss-NMR spectroscopy,^[5] calorimetry and microscopy techniques, and completed the obtained results by advanced computer calculation techniques.^[11] It is clearly evident that behavior of nanometer-sized anionic boron clusters cannot be described by paradigms and terminology established for classical ions or surfactants.^[2]

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Polyoxometalate, Octahedral Cluster and γ-Cyclodextrin. From their Primary Interactions to Supramolecular Hybrid Materials

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Polyoxometalates and octahedral metal clusters are both polynuclear ions which exhibit complementary intrinsic properties, highly appealing for developing multifunctional supramolecular systems. Investigations of their supramolecular behaviour in the presence of γ -cyclodextrin have been conducted studying structural properties in the solid state by single-crystal X-ray diffraction and specific interactions in aqueous solution using multinuclear NMR methods (including DOSY, EXSY and COSY), ESI-mass, electrochemistry and ITC experiments.¹ Solution study demonstrates clearly that pre-associations exist in solution for which the very high binding constants give preliminary arguments to state about the chaotropic nature of these polynuclear species as one of the main assembling motif.² In this communication, we report how this chaotropic effect can be used to influence significantly the self-condensation of the [MO₄]²⁻ metalate ions (M = Mo or W)³ or to produce well-ordered hybrid material derived either as supramolecular hydrogel or single-crystals.⁴ Actually, physical-chemical complementarities of the three component systems, including γ -CD, cluster and polyoxometalates open a wide scope for the design of hybrid materials that cumulate synergistic functionalities.

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Specific lon effects – Hofmeister series, extensions and beyond

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Today, the classical Hofmeister series dealing with ion properties beyond "simple" charge-charge interactions are widely understood. Especially, when these series are used together with Collins' concept of matching water affinities, they are a simple to use tool to interpret experimental results and even to predict the behavior of ions in complex systems [1].

What is more, the series can be extended and even non-ionic, polar substances can be incorporated, for example to describe there "salting-in" and "-out" effects. I will show some examples [2].

Another interesting aspect is the behaviour of charged headgroups in biological environments. For example, organophosphates show remarkable effects on proteins and can keep them in solution even under extreme conditions [3].

As it turned out in the last years, there are many specific ion effects that do not follow Hofmeister series. I will briefly mention some relevant examples [4].

Finally, I will show some examples that may be considered as "nano-ions", for example cryptates and metal complexes, as they occur in nature or can be used in photocatalytic organic synthesis [5].

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Solvation effects in the interaction of ions with interfaces: an interpretation from atomistic MD simulations

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Traditionally, ionic specificity in colloidal science has been attributed to increase/decrease in ordering and hydrogen bonding of the water molecules solvating the ions. Classically, ions were classified as water structure breakers (chaotropes) or structure makes (kosmotropes). As soon as suitable force fields were available, this interpretation was challenged by atomistic molecular dynamics (MD) simulations. Pioneering MD simulation works on ionic specificity [1,2] demonstrated that the so-called kosmotropes can actually reduce the structure of water whereas the so-called chaotropes can actually increase the structure of water [1]. An explanation of the specific effects of ions only considering the water-ion interaction is not possible [1,2]. Over the years, simulations and experiments have shown that consideration of the nature of the surface (hydrophobic or hydrophilic nature and anionic or cationic character) is essential [3]. At an atomistic/molecular level, understanding of specific ion affinity to interfaces needs explicit consideration of ion-surface-water mutual interactions involving many-body effects such as increase of water-water interaction due to partial desolvation of ions. In this contribution, we will discuss the molecular interpretation of the role of hydrophobic/hydrophilic nature of surfaces in ion-surface interaction using MD molecular simulations to interpret experimental results obtained in systems as diverse as hydrophobic and hydrophilic colloidal particles, PNIPAM chains and amphiphilic cellulose nanocrystals [3.4].

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Hydration of quaternary ammonium surfactants: ITC and DRS study of micellization

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Micelles are often regarded as a model system to study the hydrophobic effect affecting the kinetics and dynamics of chemical reactions, playing an important role in chemistry, biochemistry, and physics. In this contribution the study of the thermodynamics of micellization and the hydration in aqueous solutions for *N*-decyl-*N*,*N*,*N*-trimethylammonium chloride and four newly synthesized quaternary ammonium surfactants (Figure 1) will be presented by isothermal titration calorimetry (ITC) and dielectric relaxation spectroscopy (DRS) [1].



Figure 1. Structures of studied systems with decyl alkyl chain, R, and different functional groups, X: a) Me, *N*-decyl-*N*,*N*,*N*-trimethylammonium chloride; b) C₂OH, *N*-(2-hydroxyethyl)-*N*-decyl-*N*,*N*-dimethylammonium chloride; c) C₂OMe, *N*-(2-methoxyethyl)-*N*-decyl-*N*,*N*-dimethylammonium chloride; d) C₂OC₂OMe, *N*-(2-(2-methoxyethoxy)ethyl)-*N*-decyl-*N*,*N*-dimethylammonium chloride; e) C₂OOEt, *N*-(2-ethoxy-2-oxoethyl)-*N*-decyl-*N*,*N*-dimethylammonium chloride; d) C₂OOEt, *N*-(2-ethoxy-2-oxoethyl)-*N*-decyl-*N*,*N*-dimethylammonium chloride; e) C₂OOEt, *N*-(2-ethoxy-2-oxoethyl)-*N*-decyl-*N*,*N*-dimethylammonium chloride.

By applying a two-step micellization model [1,2] to the experimental ITC data the thermodynamic parameters and the aggregation number were determined. From DRS experiments total hydration number of the surfactant was calculated and split between the contribution of free monomers and micelles. The obtained hydration numbers of micelles are similar for all studied surfactants however the hydration numbers differ significantly for the free monomers. Introducing a polar functional group lowers the hydration of monomers.

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Inorganic Nano-Ions as Non-Amphiphilic Surfactants

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Nanometric ions (or nano-ions) with low charge density have the propensity to adsorb onto neutral hydrated surfaces or chemical functions by an entropic phenomenon, which was recently established as the superchaotropic effect.^[1, 2] In this context, the cloud point (CP) determination of the nonionic polyethoxylated surfactant C₈EO₄ (around 1% in volume) has served as a powerful tool to compare the superchaotropy of various polyoxometalates (POMs) as a function of their concentration.^[2] We expand this approach by studying the cloud point of different nonionic surfactants in the presence of various nano-ions such as POMs, dodecaborates, metallabisdicarbollides and tetraphenylborate in comparison with mixed micelles formed by adding the ionic surfactant SDS.^[3] Moreover, the respective micellar morphologies and interaction were monitored with DLS, SANS and SAXS. A strong cloud point increase, in the micromolar range, was observed for the non-amphiphilic nano-ions (Fig.1 left). This CP-increase, being comparable to the one with SDS, is due to a charging of the micelles inducing intermicellar electrostatic repulsion. In the case of the nano-ions, their adsorption onto the micellar surface is driven by their superchaotropic property, while SDS is incorporated into the micelle due to the hydrophobic effect. Additionally, upon changing the nonionic surfactant, a different behavior was observed, i.e. a closed two-phasic region appeared in the presence of nano-ions but not in presence of SDS (Fig.1 right). The distinct behavior of related surfactant systems might be due to a preferential interaction of the nano-ions with longer ethoxy chains as observed by Buchecker et al.^[4] This observed diversity shows the richness of phenomena induced by nano-ions in intriguingly simple systems emphasizing their interesting and complex behavior.



Figure 1 : Left: Cloud point evolution of the nonionic surfactant C_8EO_4 (60 mM) in the presence of the nanometric ions NaCOSAN (cobaltabisdicarbollide), NaBPh₄, HPW (phosphotungstic acid, Keggin-POM), Na₂B₁₂I₁₂ (dodecaborate) and SDS with inlet at low concentrations. Right: Cloud point evolution of the nonionic surfactant BrijO10 (14 mM, C_{18:1}EO₁₀) in the presence of HPW and SDS.

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Non-additive ion effects on collapse and swelling transitions of thermoresponsive polymers

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Most life science systems contain hydrated macromolecules whose solubility, function and stability are modulated by several small organic molecules or salts present simultaneously. While mixed solvent environments are ubiquitous in nature, non-additive salt effects are just beginning to be discovered and the molecular mechanisms involved remain largely unknown. In this contribution, we will demonstrate that non-additive effects of weakly and strongly hydrated anions drive both collapse and swelling of thermoresponsive polymers in water. We will discuss the lower critical solution temperature of poly(N-isopropyl acrylamide), poly(N,N-dimethylacrylamide) and poly(ethylene glycol) in mixed salt solutions and demonstrate that consecutive polymer collapse and swelling transitions occur in solutions with a fixed concentration of a strongly hydrated salt (Na_2SO_4 , Na_3PO_4) and a variable concentration of a weakly hydrated salt (Nal, NaSCN). The molecular mechanisms that underlie this intriguing observation will be explained based on insights obtained with molecular dynamics simulations and vibrational sum frequency spectroscopy. The observed polymer collapse transition is attributed to the partitioning of sodium ions to the counterion cloud of the strongly hydrated anion, leaving the weakly hydrated anion better hydrated. At higher concentrations of the weakly hydrated anion, it is actually forced out of solution by the strongly hydrated anion, leading to a subsequent polymer swelling transition. This new insight in Hofmeister ion chemistry is universal. It is expected to have consequences beyond the newly discovered effect on aqueous polymer solubility discussed here, for example in self-assembly and supramolecular systems.

Special Session: Nano-ions & Self Assembly ION2-3 Interactions of Cobalta-bis-dicarbollide with model biological interfaces

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Metallacarboranes (MCs) are molecular cages made of boron and carbon atoms, among which the COSAN anion $[Co(C_2B_9H_{11})^2]^-$ is the most studied. COSAN is a nanometer-sized anion composed of two nido-carborane clusters sandwiching a cobalt (III) ion. Although COSAN has no amphiphilic structure, it was shown to have surfactant properties: surface activity, foaming and formation of vesicles, micelles or lyotropic lamellar phase with increasing concentration. These properties result from the formation of intermolecular di-hydrogen bonds (C-H and B-H) and the hydrophobic effect in equilibrium with electrostatic repulsions (Fig 1a, b).^[1]

Lately MCs have attracted much attention due to their potential applications in biology.^[2] MCs possess the ability to cross efficiently biological membranes ^[3-a] and to accumulate in living cells stopping proliferation and growth.^[3-b] It is therefore essential to understand the molecular mechanisms and interactions of COSAN and its derivatives with membranes and cellular components. For this purpose, we investigate the interactions of COSAN with glucose moieties such as the octyl-glucopyranoside surfactant (C_8G_1) and with glycolipids such as MGDGsat and DGDGsat.



Figure 1: (a): Chemical structure of the cobalt-bis-dicarbollide anion (COSAN); (b), (c) and (d): COSAN and C_8G_1 self-assembly structures and their mixtures in water respectively.

Adsorption and co-micellisation between COSAN and C_8G_1 were observed and investigated at the molecular (UV-visible, NMR) and supramolecular scales (SLS/DLS, SAXS). We observed the formation of C_8G_1 decorated micelles at low COSAN content and mixed COSAN- C_8G_1 aggregates at low C_8G_1 content (Fig1 c, d). The strong COSAN- C_8G_1 interactions affect strongly both C_8G_1 and COSAN CMCs as confirmed by surface tension measurements. The COSAN-glycolipids interactions at the water/monolayer (/air) interface were analyzed through Langmuir isotherms and GIXRD/GIXOS (grazing incidence x-ray diffraction / off-specular scattering). Such non-purely electrostatic interactions between COSAN and neutral surfactants or glycolipids are a new example of the superchaotropic effect, generally observed with nanometric ions.^[4]

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Specific Effects of Trivalent Cations on the Structure and Charging State of β-Lactoglobulin Adsorption Layers

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Aqueous systems of proteins are ubiquitous in our everyday life, for example in injectable pharmaceuticals or in the form of foams in dairy products. In both cases, proteins are often used in combination with different electrolytes as excipients or additives.

In this contribution, we report on the effects of the trivalent cations Nd³⁺ and Y³⁺ on the molecular structure and charging state of β -lactoglobulin (BLG) molecules at the air-water interfaces and in the bulk solution. Both cations caused a very similar but dramatic change in the charging state. Here, ζ -potential measurements revealed a complete charge reversal from ~ -30 mV for pure BLG solutions up to ~25 mV for electrolyte concentrations >200 µM. The point of zero net charge (PZC) is observed at ~30 µM, and thereby at drastically lower concentrations in comparison to divalent cations like Ca²⁺.^[1]

Reduced electrostatic repulsive forces in the concentration range around this PZC lead to characteristic reentrant condensation with an increased optical density between 15 and 200 μ M and low colloidal stability for salt concentration between 20 and 50 μ M. Outside the latter concentration window BLG solutions are shown to have high colloidal stability.

Vibrational sum-frequency generation $(SFG)^{[2]}$ showed a comparable charge reversal at the airwater interface, at concentrations of ~40 μ M Nd³⁺ or Y³⁺. The latter is accompanied by a shift in carboxylic stretching vibrations in SFG spectra due to the formation of ion pairs. At the same concentration, the continuous decreasing surface tension reaches its minimum.

Investigations on macroscopic foams revealed structure-property relations between the interfacial charging state and the foam stability. It could be shown, that the colloidal stability of protein solutions as well as the stability of corresponding foams can be tuned by small amounts of trivalent cations. This may offer new possibilities for liquid extraction of trivalent ions.



Figure 1: Tuning of the net charge of β -lactoglobulin with trivalent cations.

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An antagonistic salt behaving as an hydrotropic solubilizer

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Hydrotropes are added component in a formulation that allow efficient solubilisation of poorly miscible solutes in water, via formation of a nanostructured solution in dynamic equilibrium. Hydrotropes reduce surface tension, but unlike true surfactants do not form micelles on their own in water(Kunz, Holmberg, & Zemb, 2016). The most studied hydrotropes such as ethanol and tert-butylacohol, while in industrial formulation sodium salicylate and tosylate are used intensively. These two electrolytes are made of one big polarisable ion and one small hydrated counter-ion, thus responding to the general definition of antagonistic ion pair as defined by Onuki and co-workers(Onuki, Yabunaka, Araki, & Okamoto, 2016).

In this talk, we will explore ternary phase diagrams obtained with salicylate. Unlike uncharged hydrotropes, there is no anomaly in calorific capacity or density in the water-rich pre-ouzo region, and therefore to "pre-ouzo effect". Unlike non-electrolyte hydrotropes, the critical point lies on the solvent-rich side of the phase diagram. A very interesting region produces intense light and X-ray scattering scattering and lies near a crystallisation boundary. The loose aggregates produced are linked to an extraordinary fluid density anomaly , and preferential solubilisation entropy stabilizes small aggregates similar to DOLLOPS ten years ago in the case of calcium carbonate(Gebauer, Völkel, & Cölfen, 2008), and extensively used as the most efficient inorganic micro-gels in art preservation, according to methods developed by Baglioni and co-workers(Baglioni et al., 2014), and could be another examples of "solvent-swollen electrolytes inorganic micelles" as proposed by several groups studying electrolyte self-assembly. We propose that these dynamic colloidal aggregates are the missing species in the Pourbaix diagram used in geochemistry, electrochemistry and inorganic chemistry.

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Headgroup-Ordered Monolayers of Uncharged Glycolipids Exhibit Selective Interactions with Ions

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Selective interactions of ions with charge-neutral saccharides can have far-reaching consequences in biological and wet-technological contexts but have so far been observed only indirectly. Here, we directly quantify by total-reflection X-ray fluorescence [1] the preferential accumulation of ions near uncharged saccharide surfaces in the form of glycolipid Langmuir monolayers at air/water interfaces exhibiting different levels of structural ordering. Selective interactions with ions from the aqueous subphase are observed for monolayers featuring crystalline ordering of the saccharide headgroups, as determined by grazing-incidence X-ray diffraction. The attracted ion species depend on the structural motifs displayed by the ordered saccharide layer [2]. Our results may constitute a basis to understand the salt-specific swelling of wood materials and various phenomena in membrane biophysics.

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Gas phase ion chemistry and soft-landing of *closo*-dodecaborate anions

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Dodecaborate anions with molecular formula $[B_{12}X_{12}]^{2-}$ (X = H,halogen), are known for their exceptional electronic properties and chemical inertness. For example, due to their high resistance to electrophilic attack, these ions are able to stabilize highly reactive cations in the condensed phase.

In the first part of the presentation, the gas phase ion chemistry of these compounds is introduced, using mass spectrometry. Bond breaking in these inert anions results in formation of electrophilic reactive sites, which contribute to the unusual reactivity of dodecaborate anions resembling highly electrophilic cations. ^[1,2] With the aid of photoelectron spectroscopy and computational investigations, we demonstrate that commonly accepted models of the electronic stability of multiply charged anions cannot explain the stability of dodecaborates. ^[3]

In the second part of the presentation, it is demonstrated how the exceptional properties of dodecaborates may be used to develop novel self-organizing layers via ion soft-landing. ^[4] Macroscopic properties of these new anion based thin film materials can be finely tuned by adjusting the properties of the mass selected anions. Possibilities to control fine structural features within these layers from the micro to nano scale are demonstrated. Moreover, it is shown that highly reactive fragment ions of dodecaborates - usually considered to be not more than elusive molecular species in mass spectrometers - can be used for bond formation in condensed phase materials. These findings provide a direct path from understanding the gas phase ion chemistry of dodecaborates to chemical synthesis in condensed phase using their reactive fragments as building blocks.

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Could Inclusion Complexes of Chaotropic Anions With Nanometer-sized Hemicucurbit[8]uril Lead to Superchaotropes?

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Solvation plays an important role in supramolecular chemistry, influencing the formation of noncovalent interactions, which are essential for the creation of molecular assemblies. Understanding the driving forces of complexation are essential for development of molecular systems that can self-organize and lead to highly efficient synthetic pathways. For example, binding of chaotropic anions to cyclohexanohemicucurbiturils allows their efficient templated synthesis in solid- and liquid phase.^[1,2] Our studies on formation of inclusion complexes of anions with chiral eight-membered cyclohexanohemicucurbituril (cycHC[8]) in protonic solvents^[3] showed, that the thermodynamic character of binding can be described through the chaotropic effect^[4]. Crystal structure of cycHC[8], obtained from methanol^[4], revealed a hydrogen-bonded network of a water molecule and nine methanol molecules surrounding two symmetry-independent cycHC[8]s. (Figure A). Upon binding of NaSbF₆ to cycHC[8], inclusion complex with chaotropic SbF₆ anion was formed, and its crystal structure^[5] (Figure B) shows that solvent molecules and cationic counter ions are disordered between equal binding cites on carbonyls of cycHC[8]. Additionally, the surface tension of methanol is affected by the presence of (PF₆@cycHC[8])⁻ complex. These observations reflect the change in the properties of solvent upon formation of inclusion complexes with chaotropic anions and the possible formation of superchaotropes. The complexation of cycHC[8] and solvation of its complexes is studied by experimental and DFT methods.



Figure: Crystal structure of (A) cycHC[8] and hydrogen bonded solvent molecules; (B) Complex of Na⁺·(SbF₆@cycHC[8])⁻, were chaotropic anion is encapsulated within the cavity and sodium cation is disordered over four positions of external rim of cycHC[8].

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Complex interaction of lanthanide salts with phospholipid micelles

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As the use of lanthanide salts in biophysical systems increases and the separation of lanthanides from nuclear and other wastes with extraction processes has become an important technological challenge, a deeper understanding of the behaviour of lanthanides at lipid interfaces is urgently needed. In this work we probe the interaction of lanthanide salts with phospholipids using aqueous micelles of the surfactant dodecyl phosphocholine (DPC), which are prototype membrane-mimetic model systems. Because more than one species exist in lanthanide salt solutions, even at the pH value of 4 used in our experiments, the major goal of this investigation is to examine which species are actually binding to the micelles. Using static and time-dependent europium fluorescence and isothermal titration calorimetry (ITC) we have obtained strong indications that both the Ln³⁺ cation and its 1:1 chloride, nitrate, or sulfate complexes bind to the micelles, whereas the lanthanide species do not interact strongly with DPC molecules below the cmc. ITC measurements reveal that the lanthanide interaction with DPC micelles increases as we move to the right of the lanthanide series and is - surprisingly - endothermic, underlying the important role of hydration effects in the interaction. The anion of the lanthanide salt strongly influences the thermodynamics: perchlorate and sulfate salts give extraordinary results, switching the interaction to exothermic. A multi-level phenomenological electrostatic model of the europium fluorescence lifetimes corroborates that in the case of nitrate salts both Ln³⁺ ions and LnNO₃²⁺ complex ions bind to the micelles. Overall a more complete molecular picture of the complexity of lanthanide-lipid interactions at interfaces is emerging from these experiments and the associated modelling effort.



Figure 1: The presentation discusses numerous proofs that both Ln³⁺ and its mono-nitrato complex binds to DPC micelles.

Ionic Boron Clusters – Anions with Unusual Coordination Properties

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Anions are not generally recognized as strongly coordinating entities in supramolecular chemistry. This is in stark contrast to cations, who have found broad application in numerous aspects of coordinative interactions.

We have discovered that dodecaborate anions associated strongly with macrocycles such as cyclodextrins (CDs) in aqueous solution.^[1-5] This is true already for the parent cluster $B_{12}H_{12}^{2-}$, and even more so for its halogenated derivatives. With the choice of the halogen, the size of cluster can be adjusted to fit a given macrocyclic host. Thus, dodecabromo-dodecaborate is the strongest host for γ -CD, whereas both the smaller dodecachloro- and the larger dodecaiodo-clusters have weaker binding.^[1] $B_{12}Br_{12}^{2-}$ shows one of the strongest interactions with γ -CD with an association constant of 960×10³ M⁻¹. Binding could be followed by isothermal titration calorimetry ITC and NMR. ¹H NMR showed that the clusters bind inside the cavity of CDs.

Substitution of the cluster with functional groups allows to use these interactions for specific purposes. Thus, we could show that the dodecaborate cluster functionalized with nitrobenzodiazol could be used as reporter in competition assays of guests binding to β - and γ -CD and allowed determination of binding constants for optically inactive guests.^[3]

The thiol-substituted dodecaborate cluster is able to stabilize gold nanoparticles and allows noncovalent surface modifications with calixarenes which are able to interact with the cluster.

We are presently expanding this work to other clusters. Decaborates (which are smaller and have less symmetry than dodecaborates) and cobaltabisdicarbollide (cosans, which are quasi-dimers of dodecaborates) are of special interest.

The strong binding expands the classical Hofmeister series of kosmotrope-chaotrope anions beyond its previous boundary. The dodecaborate ions are therefore characterized as superchaotropic anions.

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Tightly-coiled 100-nm spherical polymers of oxo-linked Keggin cluster-anions

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Soluble oligomers comprised of several polyoxometalate (POM) cluster-anions have recently been reported [1,2]. In this context, we recently discovered a method for generating covalentlylinked linear chains comprising tens of thousands of highly charged (5-) bi-functional Keggin-type cluster-anion building blocks. Along with their organic (tetraalkylammonium, $R_4 N^+$) counteractions, the linear chains form 100-nm diameter spherical coiled polymers in polar organic solvents. Although negatively charged, with zeta potential values of ca. -30 mV, in light of the large sizes of these coiled-polymer structures (with masses exceeding 20 million Daltons) electrostatic arguments dictate that most of the many tens of thousands of organic, $R_4 N^+$. counter-cations (five for each polymerized Keggin anion) must reside within the compact structures themselves. The polymers are characterized by dynamic light scattering (DLS), TEM and importantly, by cryo-TEM as well (Figure 1). Cryo-TEM imaging, a technique we have used to characterize nano-structures in their "vitrified" solution states [3], is now used to document the polymerization process, from monomeric building block, to small folded linear polymers comprized of five to 20 monomeric units, to the large compact structures shown at the right in Figure 1. To our knowledge, there is no precedent for free-standing linear inorganic polymers of this size and total charge, and the interactions and related energies responsible for their coiled structures are a current topic of investigation in our laboratory.



Figure 1. Cryo-TEM images of individual bi-functional Keggin cluster anions (left) and a 100-nm spherical coiled polymer obtained after the formation of oxo-linkages between the individual POM building blocks.

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Nanometric anions as a case study of superchaotropes

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lonic species, such as polyoxometalates (POMs) or (metal-) boron clusters, are at the frontier between ions and (charged-)colloids due to their nm size.^{1a} The large size and low charge density of these nano-ions, compared to classical ions, are responsible for a peculiar behavior called "super-chaotropy".^{1b, 2a, 3} This property refers to the surprisingly strong propensity of nano-ions to adsorb to neutral polar interfaces and to interact with macrocycles. This property results from the dehydration of (i) the weakly hydrated nano-ions, which has a reduced enthalpic cost compared to smaller ions, and of (ii) the surface (or macrocycle). A simple experimental procedure, based on cloud point measurement, was proposed lately for evaluating and classifying nano-ions according to their super-chaotropy.^{1b} The super-chaotropic behavior of nano-ions opens opportunities in separation science,^{2a} catalysis, and for the design of nanostructured hybrid materials.^{2b}



Figure 1 Nano-ions with delocalized charges, such as here POMs, strongly adsorb on neutral polar interfaces but not on hydrophobic interfaces. This property called "super-chaotropy" scales with the charge density and, to a lesser extent, with their polarizability.

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Microbubble Assisted Photo-Thermal Directed Assembly

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Micro-patterning of various materials was recently developed based on the laser-induced microbubble technique (LIMBT). LIMBT relies on the formation of a microbubble due to laser heating of a dispersion of nanoparticles (NPs) that absorb the laser light. Natural and Marangoni convection currents carry the NPs to the bubble/substrate interface where some of them are pinned. Moving the substrate relative to the laser beam results in deposition of NPs along a predetermined path. Unfortunately, for many materials this deposition is non-continuous.

We have found^[1] that controlling the construction and destruction of the microbubble through modulation of the laser enables the formation of continuous patterns by preventing the microbubble from getting pinned to the deposited material. Furthermore, we show that microstructure formation from an ion solution could be explained by a similar mechanism. Photothermal reduction of the metallic ions lead to formation of crystalline NPs. The NPs are then pinned to the bubble/substrate interface. These deposits absorb laser light, resulting in extensive local heating, which leads to fast thermal reduction of metal ions that are added as amorphous metal or metal oxides. The resulting deposition is therefore a combination of both crystalline and amorphous structures. This innovative approach could be applicable for producing thin conductive patterns and allow fabrication of microelectronic devices and sensors.



Figure 1: Illustration of the deposition mechanism from the metal ion solutions at the substrate/vapor/liquid interface.

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Special session: Wetting & Transport Surface wettability to improve heat transfer

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Heat pipe characteristics are linked to the surface properties of the diabatic surfaces, and, in the evaporator, surface properties influence both the onset boiling temperature (T_{ONB}) and the critical heat flux (CHF). In this work the effect of surface wettability in pool boiling heat transfer is studied in order to understand if there could be a path to increment heat pipe thermal performance. This work analyses the effects of surface wettability on boiling (tested fluid is pure water) and proposes a new super-hydrophobic polymeric coating which can have a very important effect in improving the heat pipe start-up power load and increasing the thermal performance of heat pipes when the flux is lower than the critical heat flux. The polymeric coating is able to reduce the T_{ONB} (-11% from 117°C to about 104°C) compared with the uncoated surfaces, as it inhibits the formation of a vapour film on the solid-liquid interface, avoiding CHT conditions up to maximum wall temperature (125°C). This is realized by the creation of a heterogeneous surface with SHS zones dispersed on top of a hydrophilic surface (stainless steel surface). The proposed coating has an outstanding thermal resistance: No degradation of SH properties of the coating has been observed after more than 500 thermal cycles.

Modus Operandi of Protective and Anti-Icing Mechanisms Underlying the Design of Longstanding Outdoor Icephobic Coatings

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Atmospheric icing became a global concern due to hazardous consequences of ice accretion on air, land and sea transport and infrastructure. Icephobic surfaces due to their physicochemical properties facilitate a decrease in ice and snow accumulation under outdoor conditions. However, a serious problem of most superhydrophobic surfaces described in the literature is poor operational durability under harsh corrosive and abrasive loads characteristic of atmospheric operation. Here we elucidate main surface phenomena determining the anti-icing behavior (Figure 1) and show experimentally how different mechanisms contribute to long-term durability. For comprehensive exploitation of those mechanisms, we have applied a recently proposed strategy based on fine tuning of both laser processing and protocols of deposition of the fluorooxysilanes onto the nanotextured surface. Prolonged outdoor tests evidence that a developed strategy for modification of materials on the nanolevel allows overcoming the main drawbacks of icephobic coatings reported so far and results in resistance to destroying atmospheric impacts.



Figure 1: The statistics of water droplets freezing on the superhydrophobic coating at different negative temperatures (left graph), ESEM image of an ice microcrystal formed at the superhydrophobic surface at a temperature of -18.8°C and relative humidity of 104% (top right image), and comparative test of superhydrophobic surface (left sample) against the reference bare aluminum plate (right sample) in outdoor conditions of dry snowfall (bottom right image).

Special session: Wetting & Transport

Transitions in the three-phase contact line motion during the pattern deposition of polymer from a volatile solution

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The motion of the three-phase contact line (CL) between a volatile solution, its vapor and a substrate, plays an essential role in the evaporative self-assembly process, and hence in the deposition of soft matter into micro and nano-structures with different morphologies.

Here we investigate the underlying connection between the state of deposition and the motion regimes of the CL of volatile polymer solutions. In particular, we study the mechanisms, which determine the different motion regimes of the CL e.g. the monotonous slip, and stick-slip motion, and we report and elucidate a new regime, the Oscillatory Wetting-Dewetting (OWD) motion.

In our experiment, we evaporate solutions of Poly-methyl-methacrylate (PMMA) and Poly-dimethyl-siloxane (PDMS) in toluene. The solutions are confined in a well-defined geometry (rectangular micro-chamber), where we align the CL linearly and adjust the system temperature, initial polymer concentration and molecular mass, and precisely determine the rate of evaporation.

We show that the state of polymer deposition and the regimes of CL motion are correlated and governed by a balance between the different mass transport mechanisms in the meniscus. We quantify the balance between polymer diffusion and convection, using a Peclet number, Pe, and the balance between the evaporative and surface energy contributions to mass transport using a Marangoni number, Ma. We demonstrate that the oscillatory wetting-dewetting motion is the consequence of an unstable balance between the rate of solvent evaporation and an outward Marangoni flow. We summarize our results in phase diagrams; one diagram presents the different morphologies of the deposit, while the other diagram visualizes the transitions between the different regimes of CL motion.



Figure 1: Temporal variations of the contact line position along the substrate (x- coordinate), which correspond to the different regimes of contact line motion.

Wetting characterization of topographically complex surfaces using Scanning Droplet Adhesion Microscopy

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Gauging the wettability of surfaces has traditionally been done nearly exclusively via contact angle measurements. These suffer from various limitations and practical challenges, and become particularly unreliable on superhydrophobic surfaces [1]. Droplet adhesion measurements have been introduced as an alternative wetting characterization method that can accommodate for greater sensitivity while having an established connection to advancing and receding contact angles [2]. In particular, Scanning Droplet Adhesion Microscopy (SDAM) can be used for systematic mapping of wettability on highly repellent, topographically complex surfaces [3].

The SDAM technique is based on a sensitive force sensor that holds a suspended liquid droplet used for probing the test surface. An automated sample stage is used for scanning the sample surface point-by-point. In each measurement point, the surface is gradually brought in contact with the droplet and subsequently retracted, while the droplet-surface interaction is measured by the force sensor down to ~5 nN force resolution.

Since SDAM does not require visual observation of the droplet-surface contact, it can be used for wetting characterization of various surfaces that have previously been challenging to probe experimentally. In this talk, I will review our recent works focusing e.g. on measuring the effects of oil lubrication on individual micropillars [4], and assessing the heterogeneity of commercial superhydrophobic coating products.



Figure 1: schematic of the SDAM measurement platform, showing the sample stage, the force sensor and the nanoliter dispenser used for forming the water droplet on the sensor disc. The cameras are used for measurement preparation and visualization purposes. Figure courtesy of Maja Vuckovac.

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Droplets on bent fibers

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Droplets trapped on fibers are part of our everyday lives: dew droplets appear on spiderwebs, rain drops are hanging under cypress leaves, water droplets are collected by cactus spines. Looking at these phenomena, scientists may wonder what is the maximum amount of fluid that a fiber can hold. Lorenceau *et al.*^[1] determined the critical volume of a water droplet hanging on a horizontal fiber.

Here, we address a similar question: we try to find out the maximum volume that a bent fiber can hold^[2]. We focus on this geometry because, in nature, some specific plants are able to hold large rain droplets thanks to their Y-shaped leaves. We try to mimic these structures using nylon fibers. We gradually bend the fibers to increase the angle between the two ends. We put a droplet on the corner and measure the maximum volume that can be reached, as it can be seen in Figure 1. It turns out that a bent fiber can hold significantly more water than a horizontal fiber. We determine the critical water volume for different fiber diameters and different angles. Finally, we propose models that are able to predict the maximum droplet size. These findings could be used in future fiber-based microfluidic devices.



Figure 1: largest soapy water droplets that can be trapped on a bent fiber. The maximum volume of the droplet strongly depends on the angle between the two ends of the fiber.

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Droplet Evaporation on Liquid-coated Substrate and Fabrication of Disk-like Supraparticles

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Drop evaporation on surfaces is extensively investigated. ^[1] Uniform deposition of materials prepared on surfaces by liquid droplet evaporation is highly recommended in bio-sensors, inject-printing and painting. ^[2,3] However, the edge-favored liquid evaporation of droplet always causes not uniform 'coffee ring' depositions, restricting practical applications. ^[4] In our work, we found that the evaporation of droplets on low-surface-tension-liquid coated substrates were completely changed with the observation under Confocal microscope. In a consequence, a uniform pattern was deposited on the substrate. We explored different thicknesses as well as different viscosities of the liquid film to determine the optimum conditions. With this method, we have printed dots with different size scaling from micro- to millimeter, which also supported us to fabricate disk-like super assemblies of micro/nano particles. Moreover, these discs can be prepared fixed to the substrate or can be collected in solution.

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Fabrication of Microsieves with integrated supportig structure for wastewater treatment

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The insufficient removal of microplastics is a problem in modern wastewater treatment. Often the plastics are passing the treatment plants and reach the rivers and seas. ^[1,2] We develop here a new way to prepare microsieves with a supporting structure that increases their stability, integrated in the sieve and created in one step: On a water surface, a pretreated polyester net is placed as supporting structure. Hydrophobic siloxane particles with 9 µm diameter are sprinkled on the water surface and are moved gently through the surface in a constant nitrogen flow to assemble in one dense monolayer on the water surface via ultrasonic treatment. The supporting structure is floating on the water surface during this process. The Particles and the supporting structure combined are embedded in a polymer membrane by spreading a solution of monomer, initiator and a water immiscible solvent on the particle monolayer, evaporation of the solvent and polymerization by ultraviolet radiation. The Particles are removed by an aqueous solution of hydrofluoric acid to generate the pores of the microsieve.

The received microsieves have an especially low flow resistance and can be currently generated in areas of nine centimeter diameter. Especially the design and the ratio of the membrane thickness to the average pore size of six micrometers leads to a high selectivity for most of the microplastics.



Figure 1: Microsieve with integrated supporting structure in a SEM – Image with a pore size of 6 micrometers.

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Penetration dynamics through nanometer-scale hydrophilic capillaries: beyond Washburn's equation and extended menisci

WET2-2

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Liquid penetration into a nanocapillary made of two parallel walls is explored by many-body dissipative particle dynamics simulations. Both partial wetting and total wetting walls are considered and the no-slip boundary condition is satisfied. The wicking velocity generally obeys Washburn's equation, but the dynamic contact angle (CA) has to be employed. The dynamic CA (θ_D) relies on the penetration rate and is always larger than the equilibrium CA. The breakdown of Washburn's equation occurs under two conditions, (i) the channel width close to molecular size and (ii) the positive spreading coefficient is large enough. Both cases come about when the wicking velocity in a nanoslit exceeds the maximum value ($\cos(\theta_D) > 1$). The failure of Washburn's equation is attributed to the invalidity of Young-Laplace equation associated with undefined meniscus. The extended meniscus will be developed as a wall of the nanoslit continues to extend outside the exit mouth. The shapes of extended menisci are discussed for both partial wetting and total wetting surfaces.



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Wettability@Al₂O₃: Adsorption of lubricant additives by molecular modeling

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In lubricant development, changes in formulations triggered by modifications of legislations, can lead to modifications of the wettability properties and the ability of the lubricant to spread over the surface. Therefore, it is important to better understand the interactions between the lubricant and the surface, and how wettability can be linked to the lubricant formulation.

In this study, we use density functional theory calculations to describe the interactions at the interface between the lubricant and the surface.

Here, we focus on industrial lubricants for applications on aluminum sheets. The major interaction of the lubricant with the surface comes from the additives it contains. For this reason, the solid-liquid interactions studied here are the ones between the surface and the functionalized head groups of the additives. This study has been conducted on a wide range of head groups: protic molecules, aprotic molecules, functionalized aromatics and phosphorous compounds.

By comparing the adsorption energies of different additives on the surface and their solvation energies in a model lubricant base oil, we aim at determining the influence of the different types of additives in the wetting process. Indeed, it has been shown that up to a certain point, solid-liquid interactions favor the wetting of the surface [1]. As a consequence, good additives should have the tendency to go to the solid-liquid interface rather than to stay in the liquid bulk. As the solvation energies obtained are quite similar (Figure 1), they are not a significant parameter to discriminate the additives, contrary to the adsorption energies. Phosphates and carboxylic acid are the most adsorbed head groups (Figure 1). For this reason, the additives containing these head groups should improve the lubricants wettability better than the ones containing head groups which are less adsorbed as water, alcohols and esters.



Figure 1: Comparison of adsorption and solvation energies for various head groups of additives: protic molecules (blue), aprotic molecules (orange), functionalized aromatics (green) and phosphorous compounds (red). * indicates dissociative adsorptions.

The results obtained are consistent with previous studies, showing that acids are improving dynamic wetting of an oil on aluminum better than alcohols and esters [2] and that phosphates are better lubricant additives that phosphites [3].

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Simulations of interface-controlled oil permeation from oil-in-water emulsions using liquid-infused membranes

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A novel type of membrane called liquid-infused membranes have been recently introduced to membrane technology. The liquid-infused pores can be opened and closed in response to external immiscible feed liquid pressure leading to an important property called gating mechanism.^[1] In the open state, the infusion liquid is still retained on the pore wall forming the so-called liquid-lined pores.^[2] Pore liquid-lining is responsible for anti-fouling properties of these membranes. The pressure responsive pores can be used for efficient sorting of fluids from a mixture based on interfacial tension. For example, in a two-phase mixture of immiscible liquids such as an emulsion, the required liquid entry pressure is different for the constituent liquids leading to the permeation of one phase and retention of the other phase. The successful permeation of the minor phase, i.e. oil from an oil-in-water emulsion using liquid-infused membranes has been experimentally investigated. [3] Here the experimental findings are complimented with many-body dissipative particle dynamics (MDPD) simulations.^[4] In the simulations, piston induced penetration of immiscible multi-component mixtures (surfactantsolution and oil) into non-infused (dry) and liquid-infused cylindrical pores is investigated. Subsequently, the amount of water permeating the pore in the non-infused (dry) and liquidinfused case is measured, and, compared to experiments.



Figure 1: A MDPD simulation snapshot of a liquid lining created by a Hexadecane-like liquid in a Krytox (K101) (yellow) infused cylindrical pore (grey + red). The Hexadecane-like liquid is assisted into the pore with the help of a piston. Here, Hexadecane and Krytox (K101) constitute an almost immiscible pair of liquids.

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Current problems in kinetics of wetting and spreading

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Background - there has been a substantial increase in the number of publications in the field of wetting and spreading since 2010 [1]. This increase in the rate of publications can be attributed to the broader application of wetting phenomena in new areas.

Aim - the current state of the art in the field of wetting and spreading will be presented.

Methods - some topics in the field are selected to be presented.

Results - these topics are as follows: (i) Contact angle hysteresis on smooth homogeneous solid surfaces via disjoining/conjoining pressure. It is shown that the hysteresis contact angles can be calculated via disjoining/conjoining pressure. The theory indicates that the equilibrium contact angle is closer to a static receding contact angle than to a static advancing contact angle. (ii) The wetting of deformable substrates, which is caused by surface forces action in the vicinity of the apparent three-phase contact line, leading to a deformation on the substrate. (iii) The kinetics of wetting and spreading of non-Newtonian liquid (blood) over porous substrates. We showed that in spite of the enormous complexity of blood, the spreading over porous substrate can be described using a relatively simple model: a power low-shear-thinning non-Newtonian liquid. (iv) The kinetics of spreading of surfactant solutions. In this part, new results related to various surfactant solution mixtures (synergy and crystallization) are discussed, which shows some possible direction for the future revealing of superspreading phenomena. (v) The kinetics of spreading of surfactant solutions over hair.

Conclusion – the importance of the topic will be presented and fundamental problems to be solved identified.

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Ink splitting and singular flows in the gravure press

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We study ink splitting and gravure cell emptying flows in a gravure printing process ^[1], with focus on the transition regime between point and lamella splitting. The fluid flow in the nip between a rotating cylinder and a co-moving planar plate has a singularity in the contact point, se fig. 1. At a given velocity, local fluid shear, pressure, and capillary forces apparently increase to infinity.

In a fluid splitting process of lamella splitting type, the nip is filled with an excess of printing fluid. In some distance from the contact point, the fluid develops a continuous meniscus, and forms transient liquid bridges between cylinder and plate ^[2]. When the excess of fluid is reduced, the meniscus is shifted towards the singularity in the contact point. Capillary and viscous forces increase at the meniscus. Finally, the transition to point splitting occurs. Each gravure cell transfers a separate drop to the substrate.

Using high-speed video analysis we study the dynamics of the fluid menisci on the convergent and divergent nip sides. In the lamella splitting regime one observes spontaneous pattern formation similar to viscous fingering. The transition between lamella and point splitting is associated with such instabilities, and fluid deposition and transfer are increasingly governed by the flow singularity and by contact line pinning of the fluid fingers at the periodic gravure pattern.

We also discuss possible mechanisms that become important in the practical case, and show that elastic deformation of even particularly rigid cylinder and substrate materials cannot be generally neglected ^[3].



Figure 1: Left: principal arrangement of the nip geometry, Right: bottom view on the fluid menisci in the nip.

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Surfactants are widely used in different branches of industry such as ink-jet printing, coating technologies and pesticides delivery in agriculture to achieve better wetting and spreading performance [1]. In last decades, a particular interest in wetting science is induced by superspreading effect taking place when trisiloxane-laden droplets meet moderately hydrophobic surfaces and spread out over them until reaching zero contact angle. Despite a number of works devoted to the investigation of superspreading, to date, its nature is still obscure [2]. In this work, for the first time, we investigate the wetting behavior and pattern formation in drying drops of nanofluids containing superspreading trisiloxane surfactants on surfaces having a water contact angle in the range of 80°-100° (Fig. 1).



Figure 1: Silwet L-77-laden quantum-dots nanofluid (surfactant concentration 0.007 wt%, particles concentration 0.5 wt%) on polystyrene surface, a – profile of the deposit showing the coffee stain, b – spreading dynamics of nanofluid, c – the coffee stain element topography (the element is shown by the solid black line on the profile of the coffee stain).

It has been found out that surfactant concentration drastically affects not only the maximum spreading diameter and coffee stain shape but also the coffee stain topography: the height of the ring as well as the frequency and the structure of the cracks over the ring.

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Static Charging of Dynamic Drops: Charge Separation as Water Moves over Insulating Surfaces

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Any time a raindrop rolls down your window, it leaves the glass with a net charge. This effect is witnessed, often with some grief, in the charging of pipetted liquids or of the aerosol mists from medical nebulizers. A number of groups have begun to decipher these charging mechanisms, suggesting that water ions are selectively left behind on the surfaces [1]. However, the literature is fairly sparse and the topic is highly charged. Little has been written about the timescales involved in electrical surface adaptation to a series of drops [2]. Additionally, it is important to distinguish between charging from drop impact on a surface, and that from continued rolling. We have developed a method for studying the individual charge from many thousands of drops rolled successively across a surface. On thin silane layers, as well as on thick layers of Teflon and PDMS, we observe temporal surface adaptation. This adaptation is dependent on such variables as drop rate, velocity, and roll distance. With the obvious prevalence and importance of water droplets in science and in society, a more thorough understanding of this topic could lead to advances in fields as wide and varied as adaptive wetting, tribocharging, electrochemistry, and renewable energy.



Figure 1: Charge separation between a moving water droplet and a hydrophobic substrate. The drop leaves the surface with a net positive charge.

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WET3-5

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Graphene oxide (GO) is the most prominent functionalized graphene derivative. A remarkable property of GO is easy hydration/solvation by vapours or liquids^[1], which results in expansion of interlayer distance. Intercalation of GO powders using liquid solvents is rather rapid and typically saturates within minutes. Likewise, the rate limiting process of solvent take-up upon imminent contact with vapours is the progressive saturation of the atmosphere with the vapour and not the insertion of its molecules into the interlayers of graphite oxide. The present structural study^[2] shows that the GO membranes are not always demonstrating the same hydration/solvation properties as precursor graphite oxides. Certain types of membranes exhibit unique hydration/ solvation properties, not found in precursor graphite oxide powders (Figure 1). In particular, both GO membranes and graphite oxides are hydrated very similarly in pure water, but insertion of ethanol and methanol into the GO membrane structure is hindered, being limited to one monolayer while in the graphite oxide powders up to 3-4 layers of these solvents can be inserted. Remarkable temperature and pressure dependent swellability features of these different microstructures will also be discussed. The tunable solvation/layer expansion properties of graphene-based membranes are relevant for various materials science applications including particle synthesis in the interlayers or membrane separation of solutes by size exclusion mechanisms.



Figure 1: Left: The temperature-dependence of the basal spacings of powdered vs membrane samples of GO immersed in alcohols. Right: X-ray diffraction image and visual and electron microscopic appearance of a GO membrane.

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Author Index

Α

Aav, Riina
Abalymov, Anatolii
Abasolo, Ibane
Abo Jabal, Mohammad226
Adroher-Benítez, Irene60
Adžić, Nataša 16
Aizenberg, Joanna198
Akamatsu, Masaaki50
Akanno, Andrew 164
Aliyah, Kinanti123
Alloyeau, Damien 123
Amer Cid, Íngrid 134
Amiar, Thanina152
Andersson, Jenny Marie12
Andersson, Jenny Marie12Angioletti-Uberti, Stefano60
Andersson, Jenny Marie12Angioletti-Uberti, Stefano60Aprile, Carmela26
Andersson, Jenny Marie 12 Angioletti-Uberti, Stefano 60 Aprile, Carmela 26 Aramaki, Kenji 84, 186
Andersson, Jenny Marie 12 Angioletti-Uberti, Stefano 60 Aprile, Carmela 26 Aramaki, Kenji 84, 186 Arbe, Arantxa 158
Andersson, Jenny Marie 12 Angioletti-Uberti, Stefano 60 Aprile, Carmela 26 Aramaki, Kenji 84, 186 Arbe, Arantxa 158 Aristegui, Christophe 143
Andersson, Jenny Marie 12 Angioletti-Uberti, Stefano 60 Aprile, Carmela 26 Aramaki, Kenji 84, 186 Arbe, Arantxa 158 Aristegui, Christophe 143 Armon, Nina 223
Andersson, Jenny Marie12Angioletti-Uberti, Stefano60Aprile, Carmela26Aramaki, Kenji84, 186Arbe, Arantxa158Aristegui, Christophe143Armon, Nina223Assaf, Khaleel220
Andersson, Jenny Marie12Angioletti-Uberti, Stefano60Aprile, Carmela26Aramaki, Kenji84, 186Arbe, Arantxa158Aristegui, Christophe143Armon, Nina223Assaf, Khaleel220Assaf, Khaleel I.205
Andersson, Jenny Marie12Angioletti-Uberti, Stefano60Aprile, Carmela26Aramaki, Kenji84, 186Arbe, Arantxa158Aristegui, Christophe143Armon, Nina223Assaf, Khaleel220Assaf, Khaleel I.205Atgié, Marina99
Andersson, Jenny Marie12Angioletti-Uberti, Stefano60Aprile, Carmela26Aramaki, Kenji84, 186Arbe, Arantxa158Aristegui, Christophe143Armon, Nina223Assaf, Khaleel220Assaf, Khaleel I.205Atgié, Marina99Audebert, Alexia104
Andersson, Jenny Marie12Angioletti-Uberti, Stefano60Aprile, Carmela26Aramaki, Kenji84, 186Arbe, Arantxa158Aristegui, Christophe143Armon, Nina223Assaf, Khaleel220Assaf, Khaleel I.205Atgié, Marina99Audebert, Alexia104Auernhammer, Günter K.203

В

Baccile, Niki	180
Baglioni, Piero	. 11, 13
Baluschev, Stanislav	57
Barwich, Sebastian	155
Bastos-Gonzalez, Delfi	209
Bauduin, Pierre	13, 222
Bazyar, Hanieh 2.	33, 234

Beaufils, Sylvie104
Bégin-Colin, Sylvie138
Ben Messaoud, Ghazi180
Berger, Rüdiger192
Bergese, Paolo 174
Berti, Debora
Bertram, Florian197
Besse, Samentha
Bešter-Rogač, Marija 159, 210
Beunis, Filip134, 151
Bharatiya, Bhaveshkumar19
Bibette, Jérôme140
Bilibin, Alexander 163
Bindgen, Sebastian37
Binks, Bernard P102, 103
Bizeau, Joelle
Björkegren, Sanna Maria Sofi 107
Blanck, Sarah
Boakye-Ansah, Stephen95
Bochenek, Steffen110, 126
Bogri, Panagiota149
Bohinc, Klemen
Boinovich, Ludmila B196, 225
Bomal, Enzo
Boniello, Giuseppe 183
Bonini, Massimo11, 13
Bordes, Romain
Borkovec, Michal6
Boshkov, Nikolai 53
Boshkova, Nelly53
Botin, Denis113
Bouwen, Thomas67
Brambilla, Giovanni 152
Braunschweig, Björn214
Bremond, Nicolas 140
Bretz, Coline

Brezesinski, Gerald	216
Bridonneau, Nathalie	184
Briscoe, Wuge	1,200
Briscoe, Wuge H 1	9, 173
Brocca, Paola	66 , 68
Bruce, Ellen E	212
Brugnoni, Monia	126
Brunet, Thomas	143
Buchecker, Thomas	222
Buchner, Richard	210
Bui, Pho T	212
Butt, Hans-Jürgen 165, 190, 192, 22	9, 238
Buzzaccaro, Stefano3	3, 161

С

Caciagli, Alessio	146
Cadot, Emmanuel	207
Callens, Michiel	151
Camerin, Fabrizio 3	6, 176
Campbell, Richard A.	164
Candau, Nicolas	181
Cano-Bonilla, Marina	49
Cantù, Laura	66, 68
Cao, Tinyang	146
Cao, Yifeng	18
Cardinaels, Ruth	144
Carl, Nico	177
Carn, Florent	184
Carreño, Aida	63
Casciardi, Stefano	70
Caselli, Lucrezia7	2 , 174
Catrysse, Leen	67
Cautela, Jacopo	175
Cazares-Cortes, Esther	74
Cerbino, Roberto	112
Champagne, Clémentine	148
Chazapi, Ioanna	219
Chevance, Soizic	62
Chiessi, Ester	14
Chirkov, Nikolai	193
Chochos, Christos	64
Cholakova, Diana	100
Chu, Kang-Ching	231
Claesson, Per Martin	190
Cloître, Michel	148
Čobanov, Isidora	159

Collard, Ylona 171, 172
Colmenero, Juan
Colombo, Gabriele
Colombo, gabriele
Constantin, Doru 123
Cook, Joanne
Corchero, Jose Luís
Córdoba, Alba63
Corvo, Laura
Couvreur, Patrick
Cox, Simon J 104
Crassous, Jerome J 175
Cremer, Paul S
Crestel, Erwan140
Cristóbal-Lecina, Edgar63
Crowley, Daniel
Cwalina, Colin

D

D'Errico, Gerardino15	4
Díaz-Riascos, Z. Vanessa	3
Danino, Dganit	8
Danov, Krassimir	7
Darras, Alexis	9
De Buyl, Pierre	7
de Campo, Liliana13	0
De Coninck, Joël 224	4
de la Motte, Hanna4	7
de Oliveira, Rodrigo J	8
Debecker, Damien	6
Debrouwere, Maarten	7
Degot, Pierre-Emile-Lucien21	5
Deguchi, Shigeru9	6
Dekker, Frans 13	1
Dekker, Riande I 108, 11	3
Del Favero, Elena	8
Del Giudice, Alessandra16	2
Del Monte, Giovanni17	6
Del Sorbo, Giuseppe Rosario 15	3
Demirörs, Ahmet Faik5	8
Demirelli, Mesut54	4
den Otter, Wouter 157, 233, 234	4
Denkov, Nikolai	0
Desmaële, Didier7	1
Deutsch, Moshe9	8
Di Cola, Emanuela	8

Diat, Olivier
Diddens, Christian136
Dimitrova, Iglika 195
Do, Thu Thi Anh 90
Doblas, David
Dombrowski, Richard156
Dong, Jun
Dorbolo, Stéphane141
Dordovic, Vladimir
Dörsam, Edgar 236
Douliez, Jean-Paul
Drummond, Carlos
Dufrêche, Jean-François
Dulle, Martin
Dunne, Fritz
Duwe, Matthias 127
Dzubiella, Joachim60

Ε

Eftekhari, Karaneh	
Ehmann, Heike M.A.	119
Eiser, Erika	146
El Maangar, Asmae	
Eliat, Pierre-Antoine	
Emelyanenko, Alexandre M	196, 225
Emelyanenko, Kirill A	196, 225
Eneren, Pinar	
Eriksson, Mimmi	
Esquena, Jordi	
Evans, Rachel Claire	
Evers, Chris	
Eyley, Sam	67

F

Faers, Malcolm A	1
Fanova, Anastasiia188	3
Faraudo, Jordi)
Fardim, Pedro	3
Farkas, Katalin	5
Farrokhbin, Mojtaba	1
Felder-Flesch, Delphine	3
Ferguson, Calum T.J24	1
Fernández-Peña, Laura164	1
Fernandez-Alvarez, Roberto 206	5
Ferreiro-Cordova, Claudia 44	1
Fetin, Petr	3
Filiberti, Zeno	3

Fleming, Robert
Fontaine, Philippe
Forg, Sandra
Forsman, Jan55, 56
Förster, Stephan 160
Frauenrath, Holger
Fresnais, Jérôme54
Frielinghaus, Henrich129
Friesen, Sergej
Frommweiler, Thomas
Furst, Eric
Fusaro, Luca

G

Gabel Detlef	220
Gadžurá Slobodon	150
Gaillard Cedric	
Calantini Luciano	162 175
Calambaak Andra	. 102, 173
Gallei, Markus	
Galli, Marco	48 , 194
Gambaryan-Roisman, Tatiana	
Gane, Patrick A.C.	190
Gao, Aiting	229
Garbin, Valeria	102
García-Aranda, Natalia	63
Garrigue, Patrick	
Garvey, Christopher J.	130
Gauffre, Fabienne	62
Gavrilova, Daria	163
Geiger, John	150
Gellerman, Gary	178
Gelli, Rita	11 , 13
Germán-Bellod, Alicia	
Girard, Luc	. 213, 222
Giuliani, Antonio	120
Gnan, Nicoletta	36, 176
Gobeaux, Frédéric	
Gochev, Georgi	
Goedel, Werner A.	. 166, 230
Goldmann, Claire	123
Gonella, Grazia	
Gontsarik, Mark	
Gonzáles García, Álvaro	131
González-Mira, Elisabet	63
González-Rioja, Ramón	63
J -	

Gonzalez-Burgos, Marina 158
Gonzalez-Garcia, Lola
Götz, Klaus
Goubault, Clement
Goujard, Sarah148
Gradzielski, Michael 105, 124, 125 , 179
Greenberg, Ehud
Griffete, Nébéwia74
Grillo, Isabelle
Grosjean, Galien 171 , 172
Grover, Liam
Gruesser, Martin117
Gubala, Dajana Magdalena 200
Guenoun, Patrick
Guidolin, Chiara101
Gutowski, Olof
Guttman, Shani98
Guzmán, Eduardo 164

Η

Haase, Martin F.	95
Hagemans, Fabian	.80,132
Hamon, Cyrille	123
Harries, Daniel	
Harrison, Kelsey	156
Harting, Jens	171
Hassouna, Fatima	87
Hayase, Haruna	51 , 84
Hellstrom, Anna-Karin	47
Hellweg, Thomas	32
Hemmette, Sylvain	189
Heunemann, Peggy	179
Hirao, Tetsuji	45
Hoehler, Reinhard	94
Hoffmann, Ingo 124,	125, 153
Hogeboom, Myrthe	108
Hohenschutz, Max	211 , 222
Hohenshutz, Max	213
Hokkanen, Matti J.	227
Holderer, Olaf	39
Holub, Karel	142
Hoste, Esther	67
Houston, Judith Elizabeth	122
Howell, Caitlin	198
Hsiao, Lilian	
Huber, Klaus	177

 Huber, Niklas
 24

 Hubert, Maxime
 171

 Hulikal Chakrapani, Thejas
 233, 234

 Hutzler, Stefan
 94

I

•	
Ikeda, Toyokazu1	21
Illés, Erzsébet	86
Imae, Toyoko	.90
Imhof, Arnout	80
Ionita, Inbal	63
Ishii, Haruyuki	81
Iván, Béla	. 86
Iwashita, Yasutaka	83
Iyisan, Banu	.57

J

Jack, Robert L
Jacob, Alan
Jakobczyk, Helene
Järn, Mikael
Jochum, Clemens16
Johansson, Thomas151
Johnson, Andrew J 173
Jokinen, Ville
Jonchère, Alban
Joseph, Pierre
Jurczyk, Tobias160

Κ

Kaabel, Sandra
Kadam, Reshma75
Kadletz, Peter
Kafle, Ananda50
Kahl, Gerhard 16
Kahn, Myrtil L 62
Kaise, Chihiro50
Kamal, Md. Arif168
Kamburova, Kamelia Pavlova53
Kamimoto-Kuroki, Junko84
Kaneko, Teruhisa
Kanno, Yuji
Kappl, Michael 165, 190
Karg, Matthias
Karpichev, Yevgen
Kasuya, Motohiro 189
Kato, Satoru

Katzarova, Maria	5
Kegel, Willem 108	8
Keiderling, Uwe	9
Keita, Camille	7
Kelly, Elaine Anne	2
Kesselman, Ellina	8
Khan, Mohd A95	5
Kimura, Yasuyuki	1
Kister, Thomas	9
Klein, Jacob	3
Koike, Ryotaro	3
Kolasinska-Sojka, Marta 182	2
Kolle, Stefan 198	3
Komarov, Kirill A 170)
Konno, Yoshikazu	4
Koos, Erin	5
Koper, Ger JM	5
Koroleva, Marina 109	9
Kosmidis-Papadimitriou, Alexandros 22	2
Koursari, Nektaria	5
Kovalchuk, Nina M 139	9
Krafft, Marie Pierre 138	3
Kraft, Daniela J	1
Kralchevsky, Peter 187	7
Kraus, Tobias49)
Krause, Patrick 124, 125	5
Kraynik, Andy94	4
Krejca, Matthias M160	5
Krickl, Sebastian	7
Kryuchkov, Nikita P 170)
Kubochkin, Nikolai	7
Kuipers, Bonny W.M 131	1
Kumagai, Akiko 178	3
Kunz, Werner	5
Kurihara, Kazue	9
Kuttich, Björn49	9
Kvasnickova, Anezka 140)
Kyrey, Tetyana 39	9

L

Lammertink, Rob	. 233, 234
Landfester, Katharina	24, 57
Lang, Christian	133
Lapeyre, Véronique	41
Larsson, Marcus	12
Lattuada, Enrico	161

Latza, Victoria M.	216
Laurenti, Marco	91,92
Laurichesse, Eric	52
Lawton, Jacob	156
Le Floch-Fouéré, Cécile	104
Lecadre, Florian	189
Lechevalier, Valérie	104
Leconte, Nadine	104
Lee, Haesoo	
Lekkerkerker, Henk N.W.	132
Leng, Jacques	143
Leontidis, Epameinondas	
Lepêtre-Mouelhi, Sinda	
Lettinga, Pavlik	133
Li Destri, Giovanni	199
Li, Yaxing	136
Liggieri, Libero	69
Likos, Christos N.	16
Lin, Shi-Yow	193
Liu, Dongsheng	146
Liu, Jie	229
Liu, Ren	146
Liu, Wendong	165
Liu, Yu	103
Llamas, Sara	164
Loehle, Sophie	232
Loh, Watson	
Löhmann, Oliver	114
Lohse, Detlef	136
Lombardo, Salvatore	
Lõokene, Aivar	218
López Cabarcos, Enrique	91, 92
Loppinet, Benoit	120
Lucio, Marlene	23
Luding, Stefan	. 233, 234
Lumay, Geoffroy	169
Lundahl, Kristina	107
Lyu, Jieli	123

Μ

Maaloum, Mounir	138
Maas, Michael	75
Macakova, Lubica	47
Macias-Rodriguez, Braulio A	145
Maeda, Miho	. 186
Maestro, Armando	. 164

Malaspina, David C	209
Malikova, Natalie	54
Maniura-Weber, Katharina	73
Manor, Ofer	226
Marecek, Vladimir	142
Marfin, Yuriy	178
Marichal, Laurent	71
Marletta, Giovanni	199
Marota-Mapa, Ludmilla	113
Marques, Eduardo F.	61
Martens, Johan A.	
Masbernat, Olivier	
Massaro, Roberta	
Matejicek, Pavel	206
Matsubara, Hiroki	105
Matthews, Lauren	173
Mechtaeva, Elizaveta	163
Medoš, Žiga	159, 210
Mees, Maarten Antoon	
Meester, Vera	132
Mehri, Tania	222
Mei, Yuan	144
·	
Meijer, Janne-Mieke	.132,150
Meijer, Janne-Mieke Ménager, Christine	.132, 150
Meijer, Janne-Mieke Ménager, Christine Mendez Gonzalez, Diego	. 132 , 150 74 91, 92
Meijer, Janne-Mieke Ménager, Christine Mendez Gonzalez, Diego Mendia, Ander	. 132 , 150 74 91, 92 158
Meijer, Janne-Mieke Ménager, Christine Mendez Gonzalez, Diego Mendia, Ander Mendoza, Paula	. 132 , 150 74 91, 92 158 106
Meijer, Janne-Mieke Ménager, Christine Mendez Gonzalez, Diego Mendia, Ander Mendoza, Paula Mendoza, Rosa	.132, 150 74 91, 92 158 106 63
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendozza, Marco	. 132 , 150 74 91, 92 158 106 63 72, 174
Meijer, Janne-Mieke Ménager, Christine Mendez Gonzalez, Diego Mendia, Ander Mendoza, Paula Mendoza, Rosa Mendozza, Marco Merckx, Wouter	.132, 150 74 91, 92 158 106 63 72, 174 67
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendozza, MarcoMerckx, WouterMerhi, Tania	.132, 150 74 91, 92 158 106 63 72, 174 67 213
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendozza, MarcoMerckx, WouterMerhi, TaniaMerlo, Josep	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 63
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendozza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, Gérard	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 63 152
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendozza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, Carine	.132, 150 74 91, 92 158 106 63 72, 174 67 67 63 63 152 232
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendozza, MarcoMerdozza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-Philippe	.132, 150 74 91, 92 158 106 63 72, 174 67 213 63 152 232 76
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendozza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, Jiarul	. 132 , 150 74 91, 92 158 106 63 63 213 63 152
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendozza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiguet, Jonas	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 63 152 232 76 165 204
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendozza, MarcoMerckx, WouterMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiguet, JonasMiller, Reinhard	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 63 152 232 76 165 204 193
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, PaulaMendoza, RosaMendoza, RosaMendoza, MarcoMerdoza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiguet, JonasMiller, ReinhardMiras, Jonathan	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 63 152 232 76 165 204 193 106
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, PaulaMendoza, RosaMendoza, RosaMendoza, MarcoMerdozza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiguet, JonasMiller, ReinhardMiras, JonathanMitsou, Evgenia	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 152 232 76 165 204 193 106 64
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendoza, MarcoMerdoza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiller, ReinhardMiras, JonathanMitsou, EvgeniaMiyawaki, Atsushi	. 132 , 150 74 91, 92 158 106 63 213 63 213 63 152 232 76 165 204 193 106 64 178
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendoza, RosaMendoza, RosaMendoza, MarcoMerckx, WouterMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiguet, JonasMiller, ReinhardMitsou, EvgeniaMitsou, EvgeniaMöbius, Matthias Enrique	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 152 232 76 165 204 193 106 64 178 155
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendoza, RosaMendoza, RosaMendoza, MarcoMerckx, WouterMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiguet, JonasMiller, ReinhardMiras, JonathanMitsou, EvgeniaMöbius, Matthias EnriqueModin, Evgeny B.	.132, 150 74 $91, 92$ 158 106 63 $72, 174$ 67 213 63 152 232 76 165 204 193 106 64 178 155 225
Meijer, Janne-MiekeMénager, ChristineMendez Gonzalez, DiegoMendia, AnderMendoza, PaulaMendoza, RosaMendoza, RosaMendoza, RosaMendoza, MarcoMerdoza, MarcoMerckx, WouterMerhi, TaniaMerlo, JosepMeunier, GérardMichel, CarineMichel, Jean-PhilippeMidya, JiarulMiguet, JonasMiller, ReinhardMitsou, EvgeniaMitsou, EvgeniaMobius, Matthias EnriqueModin, Evgeny B.Moghimi, Esmaeel	. 132 , 150 74 91, 92 158 106 63 72 , 174 67 213 63 152 232 76 165 204 193 106 64 178 155 225 149

Moncho-Jordá, Arturo	60
Mondain-Monval, Olivier	143
Montis, Costanza	72, 174
Moreno, Angel J.	158
Mourran, Ahmed	126
Murgia, Sergio	154
Murphy, Ryan P	42

Ν

N'Diaye, Marline76
Nagai-Kanasaki, Yu96
Nagao, Daisuke
Naito, Akane
Nakazawa, Hiromitsu
Narayanan, Theyencheri 115, 168
Naseri, Narges47
Nau, Werner M
Nazarova, Nadzeya 57
Nepita, Irene
Neto, Chiara 201
Neyts, Kristiaan134, 151
Nguyen, Dinh-Vu138
Nguyen, Huy 55, 56
Nieder, Jana B 23
Nikoubashman, Arash165
Ninarello, Andrea176
Noirez, Laurence
Noll, Dennis M 88, 89
Nollet, Maxime
Nomena, Emma M 111
Nordstierna, Lars 107
Noskov, Boris
Nuez, Miquel

0

O'Neill, Thomas	.146
Öeren, Mario	.218
Olsson, Ulf	.162
Orecchini, Andrea	14
Ortega, Francisco	. 164

Ρ

Paduano, Luigi	154
Pal, Antara	168
Palanisamy, Duraivelan	157
Palberg, Thomas P	113
Palmqvist, Anders	107

Pamouxoglou, Andrea149
Pan, Zhao
Papadimitriou, Vasiliki
Parakhonskiy, Bogdan 20, 167
Pasquet, Marina
Passemard, Solène63
Paunov, Vesselin N 59
Pavel, Nicolae Viorel162
Pedersen, Jan S 63
Pedersen, Jannik N63
Perez-Fuentes, Leonor 209
Perro, Adeline
Perton, Francis
Petekidis, George149
Petukhov, Andrei V132
Peyre, Véronique 54
Pezennec, Stéphane 104
Pfnür, Annemarie 88, 197
Philipse, Albert P 131, 132
Piazza, Roberto
Pichai, Supakit17
Pirolt, Franz119
Pispas, Stergios188
Pitt, William 228
Pletsa, Vasiliki64
Pomposo, José A158
Poncelet, Olivier143
Ponomareva, Ekaterina185
Poulos, Andreas149
Prévost, Sylvain
Pralits, Jan O 69
Preisig, Natalie135
Procházka, Karel 188
Procházka, Karel

Q

Qiu, Xing-Ping	82
Qiu, Yating	41
Quast, Jan-Henrik 1	27

R

Radeva, Tsetska	. 53
Radulescu, Aurel	158
Raffaelli, Chiara	. 80
Ragozin, Elena	178
Ram-On, Maor124,	125

Ramirez, Carla	106
Ramseyer, Christophe	71
Ranchon, Hubert	152
Ras, Robin H.A.	
Ravaine, Valérie	79
Ravaine, Valerie	41
Ravera. Francesca	
Real Oliveira, M. Elisabete C.D.	
Redeker. Christian	191
Reichardt. Wilfried	138
Reichow Marten	139
Ren Hao	82
Ren $\Omega_{\rm Un}$	73
Renault Jean-Philippe	71
Repetto Rodolfo	60
Paufar Mathias	118
Dozwan Kurosah	75
Rezwall, Kulosch	73 71 4
Richering Walten	110 126
Richtering, walter	110, 120
Riul, Flancesca	11, 13
Riegler, Hans	10/
	101 204
	101, 204
Robben, Bavo	134, 151
Roelants, Sophie	180
Roger, Kevin	12, 99
Rogers, Bradley A	212
Roisman, Ilja V	236
Roller, Jörg	150
Romano, Mario R	69
Rondelli, Valeria	66, 68
Rosenholm, Jessica Marianne	5
Rosilio, Véronique	76
Rostami, Peyman	203
Rouquette, Marie	71
Rouyer, Florence	204
Rovigatti, Lorenzo	176
Royall, C. Patrick	34, 44
Royo, Miriam	63
Rubio Retama, Jorge	91, 92
Rubio, Ramón G	164
Ruffino, Roberta	199
Ruiz Franco, José Manuel	36
Rumyanstev, Evgeniy	178
Ruta, Beatrice	66
Riiter Avel	162

AUTHOR INDEX

Rutkevicius, Marius	 	111
Ruzicka, Barbara	 	70

S

•	
Sadlik, Bram	151
Sagawa, Naoya	. 96
Saha, Saikat	102
Saint-Jalmes, Arnaud	104
Sakai, Hideki	. 50
Sakai, Kenichi	. 50
Sakamoto, Hiromu	105
Sakata, Osamu	.84
Salentinig, Stefan	. 73
Salinas, Nestor	106
Salmon, Jean-Baptiste	137
Salonen, Anniina	101
Salvatore, Annalisa	. 72
Samanta, Archana	. 40
Samec, Zdenek	142
Samson, Firmin	.71
Sandri, Giuseppina	. 68
Santanach-Carreras, Enric	140
Santini, Eva	. 69
Šarac, Bojan	159
Sauer, Hans Martin	236
Saveleva, Mariia	. 20
Scales, Peter J.	130
Scarratt, Liam Ronald John	201
Schäfer, Julian	236
Schaffner, Denise	138
Scheid, Benoit	141
Schindler, Torben	. 89
Schlander, Annika	. 30
Schmid, Philpp	222
Schmitt, Véronique	, 52
Schmutzler, Tilo	. 46
Schneck, Emanuel 153, 213, 2	216
Schneider, Stefan	127
Schoelkopf, Joachim	190
Schomäcker, Reinhard	.30
Schuldes, Isabel	. 89
Schulte, Marie Friederike	126
Schurtenberger, Peter	168
Schwaar, Nadine	230
Schwartz Jr., Simó	. 63
Schweinfurth, Holger	113

Schweins, Ralf		177
Sciortino, Flavien		. 62
Scotti, Andrea	110,	126
Sennato, Simona		.70
Serra, Francesca		183
Shakhman, Yuri		
Sharpnack, Lee		115
Shekhter-Zahavi, Talia		178
Shen, Yi		. 22
Sheng, Yu-Jane		231
Shi, Da		138
Shi, Yan		. 82
Shimura, Takuya		.81
Shpaisman, Hagay		223
Silvestre. Oscar F		
Silvi. Luca		114
Simmons Mark I H		139
Simon Miriam	124	125
Sirieix-Plénet Iuliette	121,	54
Skepö Marie		15
Skirtach Andre	20	167
Skovroinski Fuzébio	. 20,	38
Slavchov Radomir		195
Sloutskin Eli		98
Smith Ana Sunčana	• • • • •	171
Smoulov Stoven K		1/1
Sobhana Liji	· · · · · 27	100
Sochon Pohert	21	, 20
Soctoort Wim		175
Sofranjay Constanting	• • • • •	210
Solomon Michael	• • • • •	219
Solomona, Michael	• • • • •	. 31 179
Sololilollov, Alexey	• • • • •	1/0
Šofivico, Fabio	••••	00
Soushahàna Olivian		. 0/
Soudabere, Olivier		. 32
Soumoy, Loraine	• • • • •	
	• • • • •	. 29
Sparr, Emma	• • • • •	. 12
Statslien, Shane	••••	198
Starov, Victor	••••	235
Stebe, Kathleen J.	• • • • •	183
Steck, Katja	• • • • •	135
Stefaniu, Cristina		216
Steffen, Werner		229
Stehl, Dmitrij		. 30
Steinmann, Stephan		232

Stenqvist, Björn	175
Štěpánek, Miroslav	188
Stetten, Amy Zufall	238
Stevens, Chris	180
Stiakakis, Emmanuel	. 16
Stock, Sebastian	. 30
Stoev, Iliya	146
Stojimirovic, Biljana48,	194
Stott, Ian	187
Stoyanov, Simeon	187
Strobl, Markus	130
Strubbe, Filip 134,	151
Stubenrauch, Cosima	135
Studart, Andre	. 58
Suau, Jean-Marc	148
Sukenik, Shahar	21
Sukhov, Alexander	171
Sundblom, Andreas	107
Swan, James	31
Swerin, Agne	190
Syren, Marie	47
Szabó, Ákos	. 86
Szabo, Tamas	239
Szekeres, Márta	.86
Szuwarzynski, Michal	182
Szyk-Warszy?ska, Lilianna	65

Т

Tabakova, Nadezhda	53
Tajima, Yui	81
Takimoto, Eriko18	86
Talmon, Yeshayhu (Ishi)7, 124, 12	25
Talyzin, Alexandr2	39
Tardani, Franco	70
Tatry, Marie-Charlotte	41
Tavagnacco, Letizia	14
Tcholakova, Slavka10	00
Tein, Ying-Heng Summer 20	02
Teisala, Hannu 19	90
Teixidor, Francesc	13
Tempesti, Paolo	11
Tesler, Alexander 178, 1 9	98
Testard, Fabienne	71
Theochari, Ioanna	64
Thielemans, Wim43, 0	67
Thiesen, Peter12	27

Thiramanas, Raweewan	57
Thiyam, Priyadarshini	55, 56
Titeca, Charlotte	67
Tombácz, Etelka	86
Tomsen-Melero, Judit	63
Torres Vera, Vivan Andrea	91, 92
Tóth, Ildikó Y	86
Touraud, Didier	215
Trefalt, Gregor4	8, 194
Trindade, Suelen Gauna	93
Troadec, Marie-Berengere	62
Truscott, Tadd	228
Trybala, Anna	235
Tsao, Heng-Kwong	231
Tsirigotis-Maniecka, Marta	65
Tsukamoto, Daisuke	84
Tuccitto, Nunzio	199
Tuinier, Remco	131
Tuominen, Mikko	190
Turci, Francesco	

U

Uchman, Mariusz	
Ungaro, Francesca	
Unruh, Tobias	46, 88, 89, 197
Usher, Shane P	
Ustrnul, Lukaš	

V

118
100
144
80
78
0, 167
212
80
44
192
67
35
180
67
2, 228
31
63
111
118 100 144 80 78 0, 167 212 80 44 192 67 35 180 67 2, 228 31 63 111

Velikov, Krassimir P11	1, 145
Ventosa, Nora	63
Venzmer, Joachim	237
Vermant, Jan	1, 147
Versluis, Michel	136
Vetrano, Maria Rosaria	116
Vigolo, Daniele 2	2, 139
Vikkula, Hanna	67
Villela Zumaya, Alma Lucia	87
Vinas, Clara	213
Vitry, Youen	141
Vivian, Alvise	26
Vlug, Wessel	80
Voelker, Andreas C.	118
Voggenreiter, Markus	150
Volk, Kirsten	185
Vollmer, Doris	190
Voloschuk, Denis	109
von Klitzing, Regine 30, 3	9, 114
von Lospichl, Benjamin	179
Vraneš, Milan	159
Vuckovac, Maja	227

W

Wagner, Norman J 42, 156
Wallquist, Viveca190
Wallyn, Justine
Warneke, Jonas
Warszyński, Piotr
Watanabe, Kanako
Weaire, Denis94
Weber, Ariane
Weber, Stefan A. L
Weinstock, Ira Alan
Wellert, Stefan
Wenzl, Jennifer113
Weyer, Floriane
Whitaker, Kathryn
Whitehead, Lorne151
Wien, Frank
Wijshoff, Herman136
Wilhelm, Claire74

Wilk, Kazimiera A
Will, Johannes
Winnik, Francoise M82
Witte, Judith
Wittenberg, Christopher 113
Wlodek, Magdalena182
Woodcock, Emily152
Woodward, Clifford 55, 56
Woracek, Robin
Worsch, Peter Mario 119

Χ

Xenakis, Aristotelis	•••	 •	 		•	•		 	. 64	ł
Xing, Zhongyang			 ••	•••		•	 •	 ••	146	5

Υ

Yaghmur, Anan	73
Yakovlev, Egor V	170
Yamashita, Mika	51, 84
Yamashita, Yuji	45
Yan, Peng	82
Yeo, Reuben J.	181
Yesylevsky, Semen O	71
Yu, Jiaming	146
Yurchenko, Stanislav O	170
Yurtov, Eugeny	109

Ζ

Zaccarelli, Emanuela	. 14, 36, 176
Zanatta, Marco	14
Zech, Tobias	46, 88, 89
Zemb, Thomas	. 29, 97, 215
Zhang, Kai A.I.	24
Zhou, Quan	
Zhu, Liwen	
Zigelman, Anna	
Zinn, Thomas	115 , 168
Zontone, Federico	
Zorin, Ivan	
Zrig, Samia	
Zumbusch, Andreas	150
Zupkauskas, Mykolas	