

**Oral Presentations**  
**Monday, September 8, 2014**

***Laureate of the Overbeek Gold Medal for 2013***  
**From Micellar Solutions to Hierarchically Organized Systems - Application of Scattering Methods in Colloid Science**

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We study colloids and self-assembled amphiphilic systems with scattering techniques like small-angle X-ray and neutron scattering (SAXS & SANS) and with static and dynamic light scattering (SLS and DLS). In the beginning we focused on dilute systems only in order to facilitate data evaluation. The possibility to transform the scattering data from reciprocal space (scattering curve) back to real space (pair distance distribution function PDDF) with the Indirect Fourier Transformation (IFT) technique opened new ways of data interpretation, i.e. shape determination of monodisperse colloids like proteins. The deconvolution of the PDDF to the radial electron density distribution allowed the determination of the internal density profiles of micelles, lamellae and micro-emulsions. An important progress was possible with the incorporation of particle interaction in the evaluation technique (Generalized Indirect Fourier Transformation GIFT). This made it possible to study concentrated systems directly without dilution. It is well known that self-assembled systems can show structural changes with concentration.

When studying hierarchically organized systems one wants to determine structural details in a wide size regime. That's where the combination of SAXS & SANS with SLS and DLS becomes important. While SLS is useful to study the static structure for systems up to several micrometers in size, DLS can help to get further information about diffusion dynamics of the sample studied, including the determination of the sol – gel transition. With modern instruments such studies can be time-resolved when studying non-equilibrium systems. These experiments can also be performed in turbid samples. I shall show typical results for the different systems discussed above with special emphasis to unexpected results.

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***Invited Lecture:***

**Charging in Non-Polar Liquids: Specific and Non-Specific Effects**

Hans-Jürgen Butt, Ralf Moritz, Konstantinos Mpoukouvalas,  
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George Floudas

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Ion dissociation in non-polar solvents is still far from being fully understood. Usually it is studied with surfactants which aggregate and form micelles. Here, we report on experiments with dendrimers, where the structure is defined with atomic precision. The ion dissociation and transport properties of a series of tetrabutylammonium salts (TBA $\beta$ ) of rigidly dendronized anions with various sizes have been investigated in toluene, THF, and chloroform for a range of concentrations with dielectric spectroscopy and diffusion ordered spectroscopy (DOSY)-NMR. This is one of the first cases that one can study salts in low polarity solvents. The new synthetic approach increases the solubility and allows for investigation of both steric hindrance as well as electronic effects in producing weakly coordinating anions. We found that steric effects promote ion dissociation. In addition, fluorine substitution in the dendritic corona screens the electrostatic interactions and leads to increased dissociation. From the degree of dissociation and the measured diffusion coefficients, the free anion and cation diffusion coefficients were extracted and compared for the different dendrimer generations.

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**Supramolecular Colloids, from Intermolecular Interactions to Surface Forces**

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Colloids are commonly used as building blocks for the synthesis of advanced functional materials. To realise complex morphologies, accurate control over the specificity and directionality of the colloidal interactions is often required. This can be achieved via the functionalization of colloids with supramolecular moieties, whose interactions are well studied in bulk and dilute solutions, and are strong, directional and reversible by varying the polarity of the solvent, the temperature or by light. In this context, we propose the decoration of colloids with supramolecular moieties for the synthesis of dynamic and responsive complex materials. Our approach consists of silica particles functionalized with o-nitrobenzyl protected benzene-1,3,5-tricarboxamide (BTA) derived molecules. BTA molecules were covalently attached onto the surface of fluorescent silica particles, that remain singlets when dispersed in organic solvents. The cleavage of the protecting group by light allows to activate the short-range hydrogen-bonding interactions of the supramolecular moieties, which in turn triggers the clustering of the particles. The transition from singlets to clusters was evidenced by means of confocal microscopy. Furthermore, the binding strength was tuned with the temperature. The effect of the functionalization degree (controlled during the functionalization step) as well as the amount of active sites (controlled by the light exposure time) on the behavior of the particles was also explored. The behaviour of these supramolecular colloids demonstrates that small surface-grafted molecules can have a dramatic effect on the behaviour of colloidal particles. In summary, we combine supramolecular chemistry with colloid science in a novel approach to control interparticle interactions, which represents an elegant way to realise external control over colloidal phase behavior which could be interesting in fields where stimuli-responsive systems are needed.

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## **An Investigation of the Assembly Conditions of Colloidal Particles Under Electrical Field**

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The assembly of particles is one of the many methods for the fabrication of organized structures in the range of nanometer sizes, with a view to material science applications of which many are being explored: photonic band-gap materials, electro-rheological fluids. Colloidal suspensions are composed of particles in a solvent, where particle and solvent have different dielectric constants. In electric fields, chain-like structures form that result from a one-dimensional close packing along the electric field direction. Chain formation is followed by a coarsening of the chains into sheets. Eventually, the sheets transform into a three-dimensional crystal structure.

The colloid systems are studied in a sinusoidal alternating field as a function of electrical strength and frequencies; at high-frequencies, where particles see an average field and low-frequency where electrohydrodynamic phenomena can be observed.

We present findings on the phase transitions of functionalized porous nanoparticles in a non-aqueous solvent under an applied electric field. The colloidal systems studied are dispersions of spherical particles in PDMS or methylcyclohexanol solvents, consisting of a porous silica core, partially filled with water molecules and coated with methacryloxypropyltriethoxysilane as stabilizing layer. The softness of the interaction is tuned in this colloidal suspension by varying the silica water content.

We report a real-time, Small Angles Neutrons Scattering and dynamic rheological measurements study of the evolution of structure in the system during the particles ordering. Experiments have been performed at different water content. Water influences the multi-scale ordering response in two different ways. At low water concentrations, it enhances the response by enhancing the interfacial polarization of the particle. While at large concentrations, the response degrades due to the non-linear conductivity in the continuous phase.

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## **Glass-Glass Transition During Aging of a Colloidal Clay**

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Recent advances in the study of soft materials have led in the last decades to a deeper knowledge of equilibrium and non equilibrium states and to the discovery of new phases besides the ones commonly experienced in atomic or molecular systems. Colloidal suspensions are characterized by a variety of microscopic interactions which generate complex and exotic phase diagrams encompassing fluid, gel and glassy states and offer the possibility to study new phase and/or state transitions. Among these glass-glass transitions are quite rare to be found, especially at ambient conditions. Here we report experimental and numerical evidence of a spontaneous glass-glass transition taking place during aging of a colloidal clay. In this work we investigate the aging behaviour of a colloidal clay through a combination of dilution experiments, X-Ray Photon Correlation Spectroscopy (XPCS) [1], Small Angle X-ray Scattering (SAXS) rheological measurements and Monte Carlo (MC) simulations. Two different glassy states are distinguished with evolving waiting time: a first one, occurring at the arrest transition (after a waiting of the order of hours), is dominated by long range screened Coulombic repulsion (Wigner glass) and a second one, previously unreported and stabilized by orientational attractions between clay platelets (Disconnected House of Cards (DHOC) glass) is found at much longer waiting times (of the order of days). These findings may have relevance for applications where a fine control of the local order and/or long term stability of amorphous materials are required [2].

[1] R. Angelini et al. **9**, 10955, *Soft Matter* (2013) accepted (2014)

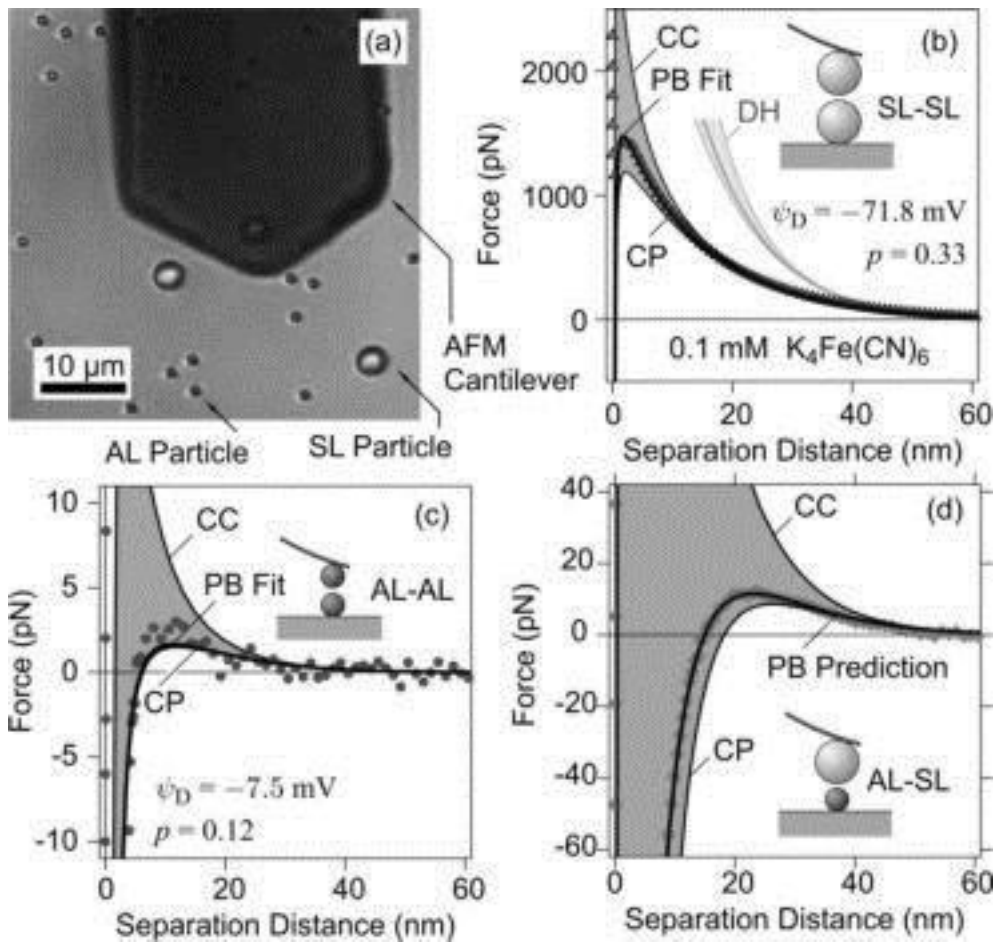
[2] R. Angelini et al. *Nature Communications*

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## **Predicting Forces between Colloidal Particles in the Presence of Multivalent Ions**

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Direct force measurements involving oppositely charged micron-sized particles were carried out across aqueous solutions of different multivalent ions with the atomic force microscope (AFM). The measurements could be interpreted quantitatively with Poisson-Boltzmann (PB) theory. Thereby, the surface potentials and regulation properties of the particles are extracted from the forces between the same types of particles. This information is then used to predict force profiles involving different types of particles without any adjustable parameters. These predictions turn out to be very accurate, which demonstrates that the mean-field PB theory is surprisingly reliable down to distances of about 5 nm. An example of this analysis is shown in Figure 1 below, which also indicates the importance of charge regulation. Similar findings were made for a wide range of different multivalent ions. The possibility to accurately predict force profiles in the presence of multivalent ions with PB theory is at odd with various reports in the literature, which state that this theory should fail in such situation due to neglect of ion correlations. We suspect that ion correlations only induce deviations at smaller distances.



F. J. Montes Ruiz-Cabello, G. Trefalt, P. Maroni, M. Borkovec (2014) Accurate predictions of forces in the presence of multivalent ions by Poisson-Boltzmann theory, *Langmuir* 30, 4551-4555

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**Stabilization of Colloids by Addition of Salt**

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We show by theory and experiment a general non-DLVO method to stabilize colloids in liquids. In this method colloidal particles that are initially unstable and sediment from the liquid are stabilized by *addition* of salt to the suspending liquid. Yet, the salt is not expected to adsorb or directly interact with the surface of the colloids. For the method to work the liquid should be a mixture and the salt need to be antagonistic such that each ion is preferentially solvated by a different component of the mixture. The stabilization can be made sensitive or insensitive to small variations in temperature, depending on the salt content, mixture composition, or distance from the mixture's coexistence line.

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**Invited Lecture:**

**Adsorption of the Cationic Surfactants CnTAB at Water/Alkane Interfaces**

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Typically, the adsorption of surfactants at water/oil interfaces is described by models developed for the most frequently studied water/air interface.

However, the presence of an oil phase leads to interaction between the hydrophobic chains of the surfactant molecules with the oil molecules [1].

On the basis of experimental data for the homologous series of alkyltrimethylammonium bromides (CnTAB) the equilibrium surface tension isotherms at the aqueous solution/alkane interface are discussed. It is shown that the adsorption characteristics are described by different thermodynamic approaches. A model which assumes the co-adsorption of alkane molecules in addition to the CnTAB molecules at the interface can describe the experimental data in the best way [2].

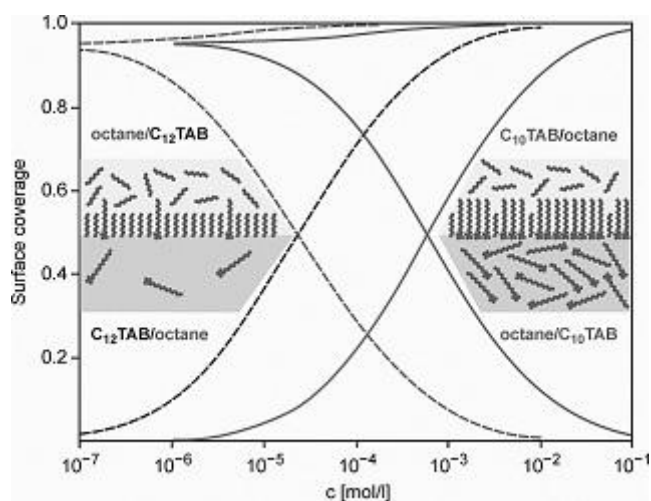


Fig. 1 Dependencies of partial and total surface coverages on the surfactant concentration in aqueous solution. Red lines, octane; blue line, C10TAB; black line, C12TAB; green lines, total surface coverages. Solid and dashed lines refer to the octane – C10TAB and octane – C12TAB, respectively.

1. V.B. Fainerman, N. Mucic, V. Pradines, E.V. Aksenenko and R. Miller, Adsorption of alkyltrimethylammonium bromides at water/alkane interfaces – competitive adsorption of alkanes and surfactants, *Langmuir*, 29 (2013) 13783–13789

2. V.B. Fainerman, E.V. Aksenenko, N. Mucic, A. Javadi and R. Miller, Thermodynamics of adsorption of ionic surfactants at water/alkane interfaces, submitted to *Soft Matter*

**Spatio-temporal Dynamics in Worm-like Micellar Systems as Studied with Rheo-NMR and Rheo-Ultrasound Velocimetry.**

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Bradley Douglass<sup>1</sup>, Marc-Antoine Fardin<sup>2</sup>, Sebastien Manneville<sup>2</sup>

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Worm-like micelles solutions (WLMs) serve as model systems to study the dynamics and non-equilibrium behavior of complex fluids [1-3]. One famous representative is 10% (w/w) cetylpyridinium chloride (CPCI) in 0.5M NaCl solution. Our aim is to further investigate the dynamics of this WLM system using two different methods, namely 2D ultrasonic speckle velocimetry (USV) [4] and Rheo-NMR velocimetry [5]. The anomalous shear banding results reported by Feindel and Callaghan [6] have been further refined. Higher spatial resolution with the Rheo-NMR technique has improved our understanding of the interface position and the variability of the shear rates in the low and high shear rate bands, as a function of the applied shear rate. As with Rheo USV, the interface position does vary with the applied shear rate while the lower shear rate was shown to be much less dependent on the applied shear rate than previously assumed. Consistently, both methods deliver a significant change in the higher shear rate. We attribute differences between the NMR and USV to instabilities (such as wall slip or elastic instabilities), which may depend on the particularities of the shear geometries. However, the overlap in results may ultimately lead to a more detailed knowledge when studying shear banding fluids with these two complementary methods.

[1] M-A. Fardin and S. Lerouge, *Eur. Phys. J. E* 35, 91 (2012)

[2] R.L. Moorcroft and S.M. Fielding, *Phys. Rev. Lett.* 110, 086001 (2013)

[3] M.R. Lopez-Gonzalez et al., *Phys. Rev. Lett.* 93, 268302 (2004)

[4] T. Gallot et al., *Rev. Sci. Instrum.* 84, 045107 (2013)

[5] P.T. Callaghan, *Rep. Prog. Phys.* 62, 599-670 (1999)

[6] K.W. Feindel and P.T. Callaghan, *Rheol Acta* 49, 1003-1013 (2010)

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**Ethanol Surface Activity in Surfactant-Free Microemulsions: Insight from the Octanol/Water Interface**

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We have recently shown that surfactant-free micelles exist in ternary octanol/ethanol/water mixtures for compositions where the ternary solution is stable, but close to the line of phase separation. In these micelle-like aggregates, ethanol plays the role of a mediating octanol hydration and is enhanced at the interface between the polar and nonpolar pseudo phases.

In this presentation, we have a closer look at the origin of ethanol's interfacial activity. For this purpose, we perform atomistic molecular dynamics simulations of planar octanol/water interfacial systems with different amounts of ethanol present. These simulations give insight into the energetic components that determine ethanol's behaviour at the interface. The simulation results point to a complex interplay of van der Waals and Coulomb interactions which determine the distribution and surface behaviour of ethanol.

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## A Reverse Micellar Mesophase of Face-Centered Cubic $Fm\bar{3}m$ Symmetry in Phosphatidylcholine/Water/Organic Solvent Ternary Systems

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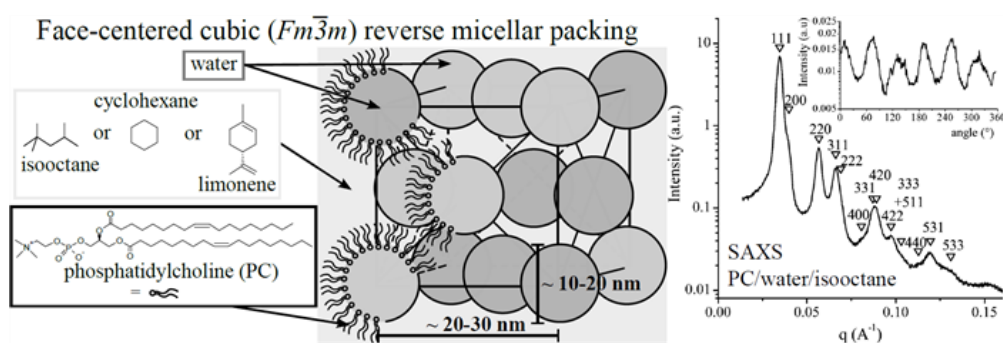
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Phosphatidylcholine (PC) forms only lamellar mesophases in water, but it can be driven to self-assemble spontaneously into nonlamellar lyotropic liquid crystalline (LLC) mesophases by the addition of a third apolar component (oil) [2]. We report the formation of a reverse micellar cubic mesophase of symmetry  $Fm\bar{3}m$  (Q225) in ternary mixtures of soy bean PC, water, and an organic solvent, including cyclohexane, (R)-(+)-limonene, and isooctane, at room temperature [1]. The mesophase structure consists of a compact packing of remarkably large reverse micelles in a face-centered cubic (fcc) lattice, a type of micellar packing not yet reported for reverse micellar mesophases.

The mesophase spacegroup was identified by Small Angle X-Ray Scattering (SAXS) based on spacing ratios and peak intensities. The variations of structural parameters point out to a classical hard-sphere phase diagram, showing an order-disorder transition  $Fm\bar{3}m$ - $L_2$  with an extended coexistence region. Form factor fitting in the pure  $L_2$  phase and in the  $Fm\bar{3}m$ - $L_2$  coexistence region yields quantitative estimations of the micellar low polydispersity ( $\sigma/R_c$  below 0.2), and PC interface rigidity  $2\kappa+\kappa'$  of 1.6-2.0  $k_B T$ .

The  $Fm\bar{3}m$  structure is compared with the non-compact  $Fd\bar{3}m$  structure found in the PC/water/ $\alpha$ -tocopherol system. The compact  $Fm\bar{3}m$  structure results mainly from (i) the release of lipid tail frustration and (ii) hard-sphere interactions between remarkably monodisperse micelles. The oil fills the geometric voids in the cell and modifies interface bending properties by penetrating the PC tails.



Acknowledgements: This study was funded by NESTEC Ltd.

[1] Martiel, I.; Sagalowicz, L.; Mezzenga, R., *Langmuir* **2013**, 29(51), 15805-12.

[2] Martiel, I.; Sagalowicz, L.; Mezzenga, R., *Advances in Colloids and Interface Science* (March **2014**, DOI:10.1016/j.cis.2014.03.005).

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## **Tuning Membrane Electrostatic Properties and Dynamics by Sphingosine and Sphingosine-1-phosphate, Two Single-chained, Oppositely Charged Bioactive Lipids**

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Sphingosine and sphingosine-1-phosphate (S1P) are known as signaling lipids which are produced from ceramide as follows: Ceramide $\leftrightarrow$ Sphingosine $\leftrightarrow$ S1P.

The ratio between these three lipids determines cell fate. In the framework of this "sphingolipid rheostat", increased level of sphingosine or ceramide promotes apoptosis, while increased S1P leads to proliferation. Although their direct interaction with signaling proteins is important, their effect on membrane physical properties might also play a role. Sphingosine and S1P are single chain lipids bearing positive and negative charge respectively at physiological pH. Our motivation is finding clues to explain the mechanisms of "sphingosine rheostat" from a physicochemical viewpoint by using artificial membranes. Large unilamellar vesicles made of egg phosphatidylcholine were used to study the sphingosine and S1P effect on (i) electrostatic properties by zeta potential measurement and (ii) membrane packing by fluorescence generalized polarization (GP) measurement using LAURDAN. First, we studied the sphingosine and S1P effects separately. GP measurement revealed that an increase of sphingosine content made the membrane more packed, while S1P had few effects on packing. Sphingosine and S1P had opposite effect on zeta potential leading to positive and more negative values respectively. This allowed us to tune the zeta potential linearly from positive to negative value, through blending the two lipids. Unlike for zeta potential, the simultaneous effect of sphingosine and S1P on lipid packing was synergistic. This shows the existence of a sphingosine-S1P cooperative effect on membrane structuring. A parallel study using giant unilamellar vesicles revealed the corresponding lipid membrane phase behaviour.

The observation that modification of the sphingosine/S1P ratio tunes both membrane charge and membrane packing might support the idea that the antagonistic role of both lipids in cell life is due in part to their effect on lipid bilayer physical properties.

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## Rings and Loops from Wormlike Micelles in Viscoelastic Solutions from Perfluoro-Surfactants

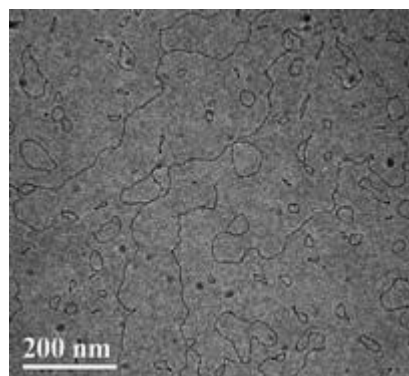
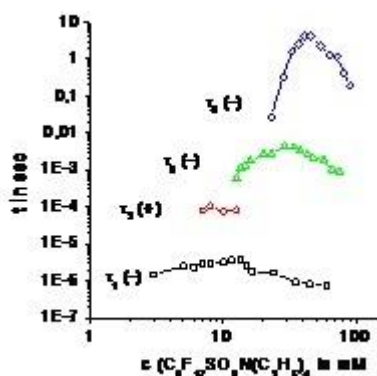
Inbal Ionita-Abutbul<sup>1</sup>, Dganit Danino<sup>1</sup>, Heinz Hoffmann<sup>2</sup>

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In a previous publication on the perfluoro-surfactant tetraethylammonium perfluorooctanesulfonate ( $C_8F_{17}SO_3N(C_2H_5)_4$ ) it was shown that the system forms viscoelastic solutions. Electric birefringence measurements on solutions of the systems revealed four different relaxation times (1) (see figure 2). The fastest relaxation time  $t_1$  around one msec was assumed to come from the rotation of small wormlike micelles with a length of about 20 – 30 nm. The  $t_3$  process was assumed to be due to a hindered rotation of somewhat longer rods.

Now, many years later, we have studied the systems with the Cryo-TEM method. The results were very surprising. Rings and loops of wormlike micelles were observed at 10mM instead of the expected small rodlike micelles (see fig. 1). Obviously the system tries to avoid endcaps and forms closed rings. The  $t_3$  process seems to come from the relaxation of the persistence length of long wormlike micelles.



1. The electric birefringence anomaly in colloidal and micellar systems, Ber. Bunsenges. Phys. Chem. 93, 184-191 (1989), M. Angel, H. Hoffmann, U. Krämer and H. Thurn

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***Invited Lecture:***  
**Structure of Networks Induced by the Capillary Force**

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The addition of small amounts of a secondary fluid to a suspension can, through the attractive capillary force, lead to particle bridging and network formation [1]. The capillary bridging phenomenon can be used to stabilize particle suspensions and precisely tune their rheological properties. This effect can even occur when the secondary fluid wets the particles less well than the bulk fluid. The properties of capillary suspensions can depend on the fluid and solid properties with even a small change to the contact angle leading to a drastic change in the rheological properties as a network transitions from contacts dominated by the strong capillary force to the weak van der Waals force. The network changes are examined using confocal microscopy and directly compared to macroscopic measurements of the shear modulus in the linear regime. A model capillary suspension composed of glass spheres in an index-matched oil with added aqueous glycerol is used in this study where the three-phase contact angle is varied through silanization. For this model suspension, capillary bridges between individual particles that create a strong space-spanning network are observed for low contact angles. At high contact angles, no network is observed and the droplets, while still attached to individual particles, do not form bridges or clusters. Transitional and cluster behavior can be observed at intermediate contact angles. The floc structure also varies with the mixing conditions where large droplets can become jammed with particles and a space-spanning capillary suspension is not formed.

[1] E. Koos and N. Willenbacher, *Science* 331:6019, 897-900 (2011).

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**The Evolving Configurations of Self-Assembled Chiral Macromolecules-  
Quantitative Measurements and Theoretical Analysis**

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Using the technique of direct-imaging cryo-transmission electron microscopy(cryo-TEM) and NS-TEM, we quantitatively study the time-evolution from micelles of **C12- $\beta$ 12** (N- $\alpha$ -lauryl-lysyl-aminolauryl-lysyl-amide) to closed nanotubes, passing through several types of intermediates. The process consists of the evolution of elongated fibrils into twisted ribbons, and later, into coiled helical ribbons.

We measure the pitch, width and radius of the ribbons at different times during their evolution. We find a good quantitative agreement between the measured data and recent theoretical predictions, derived from incompatible elasticity theory.

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**Layer-by-Layer Nanostructured Adhesives of Poly(Allylamine Hydrochloride) and Hyaluronic Acid with Wet Adhesion and Toughness Superior to Wet Adhesion in Bone**

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Andrew Marais<sup>1</sup>, Emil Gustafsson<sup>1,2</sup>, Lars Wagberg<sup>1,2</sup>

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Layer-by-Layer (LbL) assemblies of poly(allylamine hydrochloride) (PAH) and hyaluronic acid (HA) were fabricated in order to study their wet adhesive behavior. The film characteristics were investigated by AFM, QCM and DPI to understand the inherent surface structures during the assembly process. Adhesion of these systems was evaluated with colloidal probe AFM to understand the correlation between the structure of the film and the energy required to separate these LbL assemblies. We describe how the conditions of the LbL fabrication can be varied to control the adhesion between films. The characteristics of the film formation are examined as a function of ionic strength during the film formation. The dependence on contact time and LbL film thickness on the critical pull-off force and work of adhesion are discussed. Specifically, by introducing sodium chloride (NaCl) in the assembly process, the pull off force can be increased by a factor of 10 and the work of adhesion by two orders of magnitude. Based on these results we discuss how the fabrication procedure can create low or highly adhesive interfaces.

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## Characterizing and Tracking Colloidal Particles Using Image Analysis

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Colloidal particles are widely used in pharmaceuticals, flow cytometric assays, biophysics, liquid toners and electronic inks, photonics and soft condensed matter. In many of these applications it is desired to know accurate particle properties such as 3D position, orientation, size, refractive index, shape and electrical charge, properties of coatings on these particles or statistical properties of many particles. We demonstrate a method based on Fourier-Bessel (FB) image moments. In this method particle images obtained by classical white light, fluorescence, confocal microscopy or any other imaging technique are decomposed into a set of 2-dimensional orthogonal FB functions with their weights, the FB coefficients. Since each image can then be represented by a point in the multidimensional space of FB-coefficients the mathematical processing becomes much easier compared to analyzing the original images. Many images of a particle at different -positions with respect to the plane of focus result in a point cloud, a 'fingerprint', that accurately reflects its size, refractive index. Figure 1 illustrates the basic classification of spherical colloids (PMMA and PS with different sizes) depending on their size and refractive index. An accuracy of 1% in size and 0.2% in refractive index is achieved from a single image, comparable to holographic microscopy techniques [1]. A second illustration of the method is the measurement of the retardation force in nonpolar liquids [2].

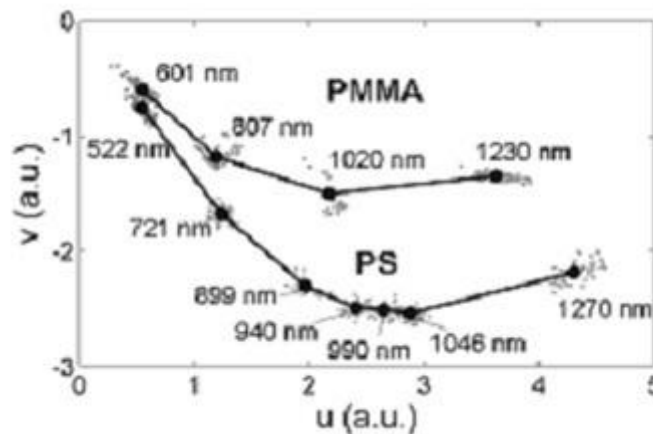


Fig. 1 Classification of individual colloidal particles depending on their refractive index and size.

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### **Rigid Unconventional Amphiphiles from Bile Salts**

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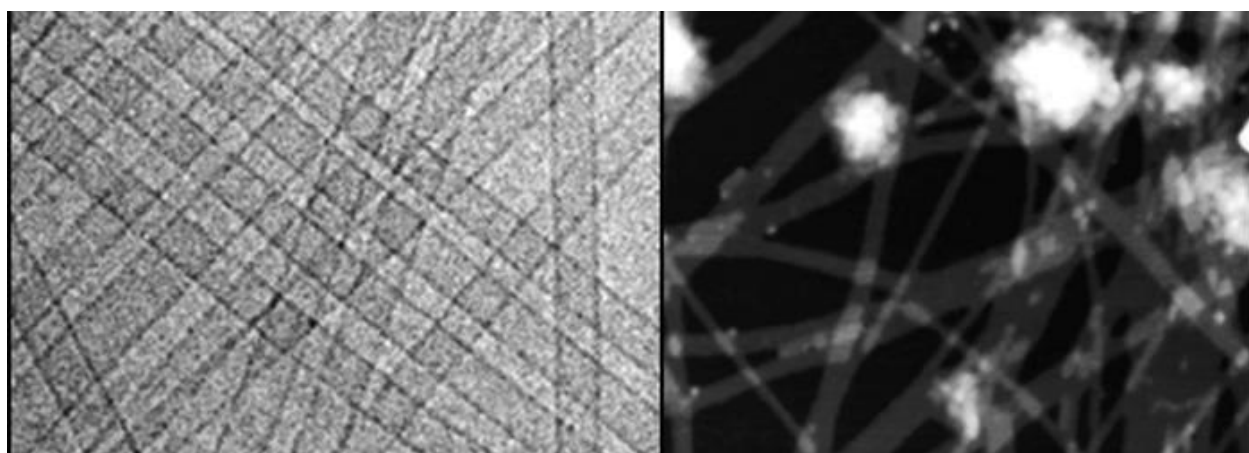
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Bile salts (BSs) are biological surfactants that have a rigid steroid skeleton, carrying hydroxyl group(s), and a charged head on the lateral chain. Due to their rigidity and their uncommon distribution of hydrophobic and hydrophilic regions BSs self assemble in peculiar supramolecular arrangements that are particularly ordered and not rationalized on the basis of the conventional geometric rules of surfactant packing. It has been shown that rigid surfactants with new amphiphilic structures and self-assembly properties can be synthesized starting from bile salts as substrates.[1-5] For example, surfactants showing thermo- or pH-responsive self assembling in tubular aggregates were prepared,[1,2] whereas mixtures of anionic and cationic forms of these derivatives were reported to form catanionic tubules with controlled stoichiometry.[3] Recently, new amino-acid or sugar-substituted derivatives have been also synthesized that form gels of extremely narrow hollow fibers [4] or monodisperse single walled tubules via scrolling of layers (Figure).[5] Self-associating molecules have shown a growing interest in the last decades for their employment in nanotechnology. The reported results demonstrate that bile acid derivatives could provide molecules with uncommon and versatile aggregation properties that could open up the possibilities for designing new nanostructured biomaterials.



Supramolecular structures of bile salt derivatives

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***Invited Lecture:***

**Nanostructured Fluids Based on Degradable Nonionic Surfactants for the Removal of Polymer Films from Works of Art**

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Nanostructured fluids containing anionic surfactants are among the best performing systems for the cleaning of works of art [1, 2]. Though efficient, their application may result in the formation of a precipitate, due to the combination with divalent cations that might leach out from the artifact. We propose here two new aqueous formulations based on CE<sub>j</sub> nonionic surfactants, which are non-toxic, readily biodegradable and insensitive to the presence of divalent ions. The cleaning properties of water/nonionic surfactant/2-butanone (MEK) were assessed both on model surfaces and on a XIII century fresco that could not be cleaned using conventional methods. Structural information on the nanofluids has been gathered by means of small-angle neutron scattering, dynamic light scattering and nuclear magnetic resonance with diffusion monitoring. Beside the above-mentioned advantages, these formulations turned out to be considerably more efficient in the removal of polymer coatings than those based on anionic surfactants. Our results indicate that the cleaning process most likely consists of two steps: initially, the polymer film is swollen by the MEK dissolved in the continuous domain of the nanofluid; in a second stage, the surfactant aggregates come into play by promoting the removal of the polymer film with a detergency-like mechanism. The efficiency can be tuned by the composition and nature of the amphiphiles and is promoted by working as close as possible to the cloud point of the formulation, where the second step proceeds at maximum rate.

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***Using Capillary Forces to Tune Stability and Flow Behavior of Food Suspensions***

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In particulate food systems the rheological behavior is strongly influenced by particle-particle interactions. Recently, we have shown that adding a small amount of an immiscible fluid to a suspension can lead to particle bridging and network formation [1]. This effect occurs both if the secondary fluid wets the particles better or worse than the bulk fluid. The capillary bridging phenomenon can be used to stabilize particle suspensions and precisely tune their rheological properties. This allows stable food products to be created without emulsifiers or stabilizing agents, as shown here for starch and cocoa suspensions [2]. The stability and the strength of suspensions highly depends on the surface properties of the particles and the wetting and re-wetting behavior of the fluids with the particles. Even a slight shift in wetting behavior results in a strong change in flow behavior.

In oil continuous suspensions of hygroscopic particles that have been conditioned over water, the network induced by capillary bridges forms spontaneously and results in the same yield stress as if the water is added to the suspension of dry particles. This demonstrates that, in contrast to Pickering emulsions, the formation of capillary suspensions is an energetically driven phenomenon. The presence of aqueous capillary bridges between cocoa particles also improves the heat stability of model chocolate systems. Water continuous suspensions can potentially be used to design novel low fat food products. We have modified suspensions of cocoa particles in water with trace amounts of an appropriate oil to achieve texture and flow properties of regular fat continuous cocoa spreads.

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### **Are Simple Fluids Complex?**

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Simple fluids like for instance aqueous solutions of common hydrophilic well soluble small organic molecules, inorganic salts or mixtures of water with other freely miscible liquids appear to be not so simple. Long-lived mesoscale (larger than molecular scale but smaller than macroscopic scale, typically  $\sim 100\text{nm}$ ) structures/inhomogeneities were evidenced in these systems by methods of static and dynamic light scattering [1]. Kinetics of the formation of these structures upon mixing was also investigated [2]. The time scale on which these mesoscale structures develop in various systems varies from seconds to days. A detailed classification of systems with respect to the capability of formation of such structures was performed (almost 100 different solute/solvent pairs) [3]. Very recently [4], it was possible to visualize these structures as well as their Brownian motion by optical microscopy in the laser beam. It was also proved that these are not nanobubbles [4]. The mystery of the origin of such mesoscale structures was successfully revealed so far in one class of systems [5]. It was proved that mesoscale structures in alcohol/water mixtures originate from mesophase separation of minority components. Chemical compounds used in everyday life and research practice (like for instance alcohols) are in fact multicomponent mixtures of the main component and minority components (unwanted admixtures, impurities). Upon mixing with water, minority components of mainly hydrophobic character (initially molecularly dissolved in alcohol) segregate into well-defined long-term stable mesoscale structures (nanoparticles or rather nanodroplets). A new term of "mesoscale solubility" can be introduced.

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**Decontamination of Sorptive Surfaces by Sugar Surfactant Based Microemulsions, Study of Wetting and Extraction Properties**

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Due to their soft and “green” performance with structural stability in a wide temperature range<sup>1</sup>, sugar surfactant based microemulsions are promising carrier media for the decontamination of sorptive hydrophobic surfaces (interior and exterior technical equipment, human skin) exposed to highly toxic and lipophilic compounds, such as chemical warfare agents, pesticides or toxic industrial compounds. The main advantages of the sugar surfactant based microemulsion rely on their ability to extract out of a surface and simultaneously transform the soluble toxic compounds into innocuous products. The aqueous phase is used as host medium for the enzyme Diisopropyl fluorophosphatase (DFPase) which efficiently hydrolyses organophosphates<sup>2</sup>. Beside the kinetics of the enzymatic degradation of the toxic organophosphate compounds, the decontamination efficiency of the microemulsion is also determined by two major factors: 1) the ability of the microemulsions to wet and eventually penetrate the sorptive hydrophobic surfaces and 2) the capacity to extract the lipophilic contaminant out of the surface and to solubilize it in the oil phase of the microemulsion. Here, we discuss extraction properties and wetting behaviour of sugar surfactant based microemulsions of different microscopic structures on model and realistic surfaces with smooth and porous structures and different hydrophobicities. The extraction capacity of different microemulsion structures was investigated by HPLC and confocal microscopy using a series of test molecules (ethyl salicylate fluorescence dyes). Extraction out of sorptive surfaces is strongly affected by the structure of the microemulsion, where an effective extraction of the model molecules is achieved by the employment of bicontinuous microemulsions.

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***Keynote Lecture:***

**Smart Complex Fluids Based on Aqueous Solutions of Antennary Oligoglycines**

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Aqueous solutions containing two-, three- or four-tailed oligoglycines are investigated in view of potential environmental and biomedical applications. The oligoglycine molecules of this type are known to self-organize into supramolecular assemblies in aqueous media: hydrophilic nanoplateforms (tectomers), vesicles, etc. The innate reason for the onset of the self-assembly is the formation of a highly cooperative system of intra- and intermolecular hydrogen bonds. We present a combined theoretical and experimental procedure, including numerical modeling of the configuration and stability of the bulk nanoaggregates, studies on the distribution of the self-assemblies by size and charge in the solution bulk, examination of the properties of interfacial layers at the solution/air boundary and of drainage characteristics of microscopic foam films.

The aqueous solutions of this type of substances are smart complex fluids whose properties may be finely tuned by the change of pH in the system, and/or the addition of charged entities: low-molecular-mass electrolytes, or high- molecular-mass substances. The reported data also suggest that the self-assembled nanostructures of antennary oligoglycines could be used as indicators and captive agents for trace quantities of dangerous substances of biological origin (e.g. endotoxins) in aqueous media.

**Acknowledgements:**

Partial financial support of Bulgarian Ministry of Education, Youth and Science through Project BG 051PO001 - 3.3.06 – 0038 is gratefully acknowledged. The authors thank Mrs. Zhana Ivanova for technical assistance. The investigation is performed under the umbrella of COST Action MP 1106 "Smart and green interfaces- from single bubbles and drops to industrial, environmental and biomedical applications".

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## Critical Parameters in Exfoliating Graphite into Graphene

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Graphite exfoliation into few-layers graphene sheets (GS) is an appealing source of graphene: environmental-friendly, low-cost and low-energy. We obtained relatively high GS concentrations in water ( $0.7\text{mg}\cdot\text{mL}^{-1}$ ) by optimizing the nature of dispersant and the ultra-sonic generator intensity. We employed a wide range of dispersant types: anionic, cationic, and nonionic surfactants, and found that neither the polarity of the dispersant nor its surface tension have a clear effect on the GS concentration. In contrast, the nature of the hydrophobic part of the dispersant strongly affects the dispersion quality. The dispersant Triton X-100 gives the highest GS concentration since it includes a benzene ring with strong  $\pi$ - $\pi$  interactions with the aromatic structure of the GS. We found that a multi-step sonication procedure involving both tip and bath sources considerably enhances the yield of exfoliated GS. Tip sonication (TS) and bath sonication (BS) differ considerably in the power they supply. It is therefore expected that the substantially higher power of TS would be more efficient than the weak BS. However, when comparing the efficiency of either TS or BS alone for the same sonication energy, TS is the least efficient option, while the weaker BS leads to a much higher GS concentration. Still, combining the two sources gives the highest GS concentration. This marked difference is ocularly visible: a much darker supernatant (higher GS concentration) is obtained by TBT than by BS alone. In order to characterize the GS, we used Raman spectroscopy and transmission electron microscopy, which indicates few-layers graphene patches of  $\sim\mu\text{m}$  lateral dimension.

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## **Non-NIPAM Based Microgels: Tuning the Volume Phase Transition by Copolymerisation and by Particle Architecture**

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Over the last decade smart microgels have been increasingly recognized as potential building blocks for photonic materials, catalytic carriers and sensors.[1] This applicability is based on the fairly unlimited tuning possibilities of swelling properties as well as scattering properties of those particles. The present contribution studies *non*-(*N*-isopropyl acrylamide)-based core-shell microgels that exhibit a linear thermoresponsive behavior in a temperature range between 25°C and 40°C. It is the combination of distinct materials in core and shell, that gives the particles this unique property. For the first part of our study we synthesized statistical copolymers from *N*-*n*-propylacrylamide (NNPAM) and *N*-isopropylmethacrylamide (NIPMAM) and study their behavior by means of scattering techniques [2]. Moreover, we have synthesized core-shell microgels from these monomers with differently cross-linked cores. This approach was inspired by the work of the Richtering group[3]. Photon correlation spectroscopy allowed us to study the temperature dependent swelling, which revealed a significant influence of the core properties on the overall core-shell behavior. A major finding of these experiments is that the swelling becomes linear dependent on temperature and the crosslinker content of the core is directly related to the linear response. The core-shell particles behave piezo-like and might have potential as actuators [4]. The internal structure of the particles is followed by means of small angle neutron scattering (SANS) revealing heterogeneities during the transitions of the NNPAM shell.

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## **Nanoparticle Adsorption and Crossing of Fluid Interfaces**

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Solid micron- and nano- particles have been extensively used to stabilize dispersions such Pickering emulsions and particle-stabilized foams. In many cases, particle's adsorption onto the fluid interfaces represents a limiting step for the stability of the dispersion since adsorption can be very slow or even hindered by interfacial potential barriers. In the first part of the talk, I will show experimental evidences on the slow dynamics of nanoparticles at the interface and the role of colloidal forces and wetting on the free energy profile across the interface. A step beyond the understanding of particle's adsorption onto the interface is the control of nanoparticle crossing of liquid-liquid interfaces. The second part of the talk discusses experiments and models describing the adsorption-desorption phenomena, which result in the phase transfer of nanoparticles from oil to water and *viceversa*. Gold nanoparticles coated with stimuli-responsive polymer transfer from water to oil and from oil to water across the planar interfaces when environmental parameters are slightly changed. The oil to water transfer occurs when the temperature is reduced below 5 °C, while they transfer from salty water to oil when the environmental temperature returns to room temperature. The water-to-oil particle transfer is dictated by the ionic strength of the aqueous phase. The transfer mechanism disparity for the two directions during NP crossing of oil–water interfaces result from an intricate interplay of interfacial interactions and transitions. Among the different experimental tools used for the investigation, multiple angle of incidence ellipsometry was applied to in situ assess the contact angle ( $\theta$ ) and surface coverage of nanoparticles as small as 18 nm at water-oil and water-air interfaces.

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## Magneto-responsive Micelles, Vesicles and Solid Lipid Nanoparticles: Properties and Uses in Silica Magnetisation

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Tuning magnetic properties is a challenge in advanced materials research, for various applications including high storage capacity media, diagnostics, imaging, hyperthermia probes or targeted delivery. Most of magnetic systems consist of either molecular nanomagnets ( $n \approx 30$  atoms) or magnetic nanoparticles ( $n = 100-1000$ ). Very recently, colloidal systems (*i.e.* micelles, micro-emulsions and emulsions), based on magneto-responsive surfactants were reported as being able to bridge this gap, allowing thus fine control upon the cluster size  $n$ , whilst combining magnetic ordering with low-density and electrical insulation [1]. Herein will be presented novel contributions on magnetic surfactants that are able to form either vesicles or solid lipid nanoparticles. Straightforward applications of these systems might be found in magneto-responsive drug delivery. Moreover, hexagonally ordered meso- and meso-macroporous materials with magnetic properties could be achieved by using magnetic surfactants as structure directing agents of silica [2]. Finally, it will be shown that magnetic properties of the self-assembled surfactants and of the resulting materials are highly dependent on the molecular organization system and on confinement of the metallic centres, respectively.

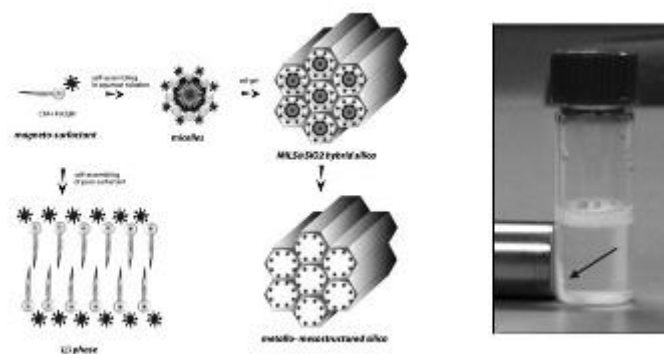


Figure 1: Imprinting pathway with magneto-surfactants of magneto-responsive porous silica

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## **Phase Behavior of a Soft Colloidal Model System studied by High-Resolution SANS**

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The structure and phase behavior of an ultra soft colloidal model system was studied by small angle neutron scattering. As a model system we have chosen polymeric micelles prepared from n-octacosanyl-poly(ethylene oxide) (C<sub>28</sub>-PEO) block copolymers in aqueous solution. The C<sub>28</sub>-PEO block copolymer forms micelles with starlike structure where the aggregation number, the size and the softness can be tuned by varying the PEO length of the polymer. Time-resolved SANS has shown that at low temperatures (15 °C ) micelles are almost frozen, whereas at higher temperatures (60 °C) the system is dynamic, i.e. an existing fast exchange of single chains. These properties allow to prepare thermodynamically stable micelles which were taken as model system for soft colloids. The system was systematically studied as a function of concentration and PEO chain length (5, 10 and 20 Kg/mol) by SANS. In the dilute limit we have determined the single micellar properties. At intermediate concentrations below the overlap concentration,  $c^*$ , SANS curves develop a structure factor peak revealing a liquid-like organization in solution. In the gel state above  $c^*$  higher order structure factor peaks were observed indicating crystalline order in micellar solutions. Using high resolution (HR)-SANS (wavelength spread  $\approx 5\%$ ) the crystalline structure of the C<sub>28</sub>-PEO5 at concentrations up to twice  $c^*$  was identified as fcc. By further increasing  $c$  a transition to bcc (bco) occurs. Micelles prepared from C<sub>28</sub>-PEO10 and C<sub>28</sub>-PEO20 only show bcc structures in the studied concentration range. The sequence of crystalline structures were found to be in excellent agreement with a theoretical phase diagram derived for star polymers, based on an ultrasoft interaction potential. Details of this study will be presented.

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### Transport of Charged Inverse Micelles in Response of Switching Voltages in Non-Polar Liquids

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The electrical behavior of surfactant added non-polar liquids is governed by the presence of charged inverse micelles. For surfactants like PIBS the transportation of charged inverse micelles from  $0 \rightarrow V$  and from  $V \rightarrow 0$  has been studied using transient current measurements<sup>1,2,3</sup>. The main contributions to these currents are due to drift and diffusion of charged inverse micelles. Now, after steady-state is reached in the polarizing step ( $0 \rightarrow V_1$ ), the transition from  $V_1 \rightarrow V_2$  is investigated with surfactant PIBS (OLOA 11k) in dodecane, which is relevant for the switching of colloidal particles in electronic inks. For low voltages ( $|V_2| < 10V$ ) the current measurements upon switching from  $V_1 \rightarrow V_2$  are in good agreement with simulations of the Nernst-Planck-Poisson equations (see Fig. 1). The shape of the currents can be understood from dynamic space-charge effects related to the switching of charged inverse micelles from within the diffuse double layer at one electrode to the other electrode. The first part of the measured currents is typically also well understood for higher voltages. However, for increasing amplitude of the voltage  $V_2$  a peak in the measured currents occurs earlier than expected, which is related to electrohydrodynamic effects speeding up the switching of charged micelles.

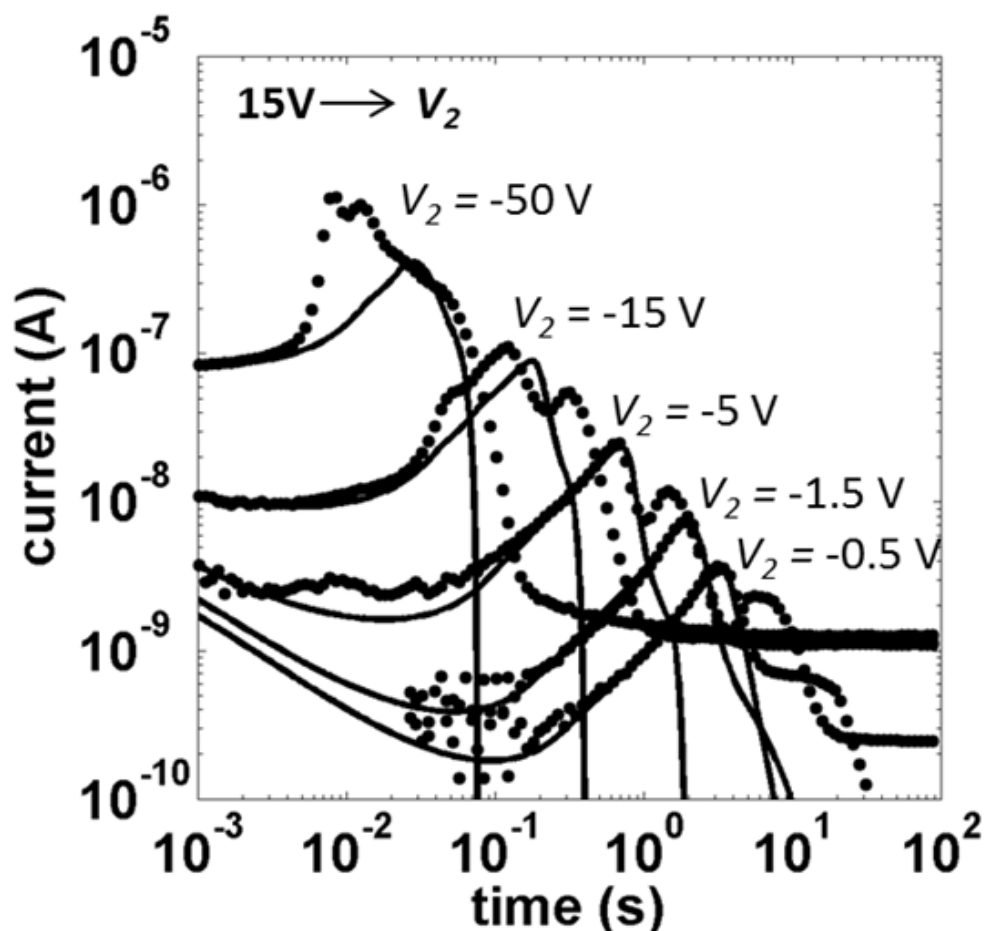


Fig.1 Transient current measurement for voltages going from  $V_1=15V$  to  $V_2=-0.5, -1.5, -5, -15$  and  $-50V$ . The measurements (dots) and simulations (lines) shows a good agreement at short times and low voltages.

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## **Kinetic Modeling of Micellization and Relaxation in Solutions with Coexisting Spherical and Cylindrical Micelles at Arbitrary Initial State**

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This work continues a numerical kinetic modeling of temporal behavior of concentrations of surfactant monomers and aggregates in solutions with coexisting pre-micellar aggregates, spherical and cylindrical micelles started in the serial of our papers<sup>1-3</sup>. Our analysis is based on a discrete form of the Becker-Döring kinetic equations for surfactant aggregation in polar solvent with the Smoluchowsky diffusion model for the attachment rates of surfactant monomers to surfactant aggregates with matching the rates for spherical and large cylindrical micelles. Here we report the kinetic regularities of micellization and relaxation at arbitrary initial state of the micellar system, when final equilibrium state of the system can be considerably different from the initial one. Thus we consider the non-linear effects at self-aggregation which can not be described within the frameworks of linear relaxation approach. The results of our computations have been compared with the analytical ones (known in the limiting cases from solutions of the continuous Becker-Döring kinetic equation) and demonstrated a fair agreement even in the vicinity of the  $cmc_2$  where the analytical theory loses formally its applicability.

This work was supported by St. Petersburg State University (grant 11.37.183.2014) and grant RFBR 13-03-00991a.

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## **Penetration of DPPC Membranes by *Quillaja* Bark Saponin**

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Despite a growing number of present and prospective applications of saponin-rich extracts from the bark of *Quillaja saponaria* Molina tree (*Quillaja* Bark Saponin, QBS), details of their interaction with biological membranes are still missing. Many saponins are known to lyse erythrocytes (haemolysis), and this property is often linked with their affinity to cholesterol [1]. Nevertheless, in some cases strong effect of saponins on cholesterol-free membranes have been observed [2], suggesting that saponins may interact also with other bilayer components, e.g., phospholipids.

In this contribution the interaction between a model phospholipid 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and QBS will be described. Surface pressure relaxation and surface dilatational rheology complemented with neutron reflectivity (NR) were employed for this purpose. In contrast to synthetic surfactants of similar surface activity (SDS, CTAB, Triton X-100), QBS does not destroy DPPC monolayers, but penetrates them, improving their surface dilatational elastic properties even in the highly compressed solid state. The dilatational visco-elasticity modulus increases from 204 mN/m for pure DPPC up to 310 mN/m for the QBS-penetrated layers, while it drops to near zero values in the case of the synthetic surfactants. The estimated maximum insertion pressure of QBS into DPPC monolayers exceeds 50 mN/m.

**Acknowledgements:** This work was financially supported by the Polish National Science Centre, grant no. DEC-2011/03/B/ST4/00780 and COST CM1101 Action

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***Invited Lecture:***

**The Effect of the Bile Salt Sodium Glycodeoxycholate on the Association Behavior of PEO-PPO-PEO Triblock Copolymers**

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Malabsorption of bile acids at the end part of the small intestine causes bile acid diarrhea in human body. The aim of this study is to investigate the possibility of using nonionic triblock copolymers based on poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) instead of present sequestrants in the treatment of this disease. The influence of a bile salt, sodium glycodeoxycholate (NaGDC), on the association behavior in water of three copolymers with different block lengths of PEO and PPO (EO<sub>19</sub>-PO<sub>29</sub>-EO<sub>19</sub> = P65, EO<sub>20</sub>-PO<sub>69</sub>-EO<sub>20</sub> = P123 and EO<sub>100</sub>-PO<sub>65</sub>-EO<sub>100</sub> = F127) has been studied by means of light, X-ray and neutron scattering in combination with differential scanning calorimetry. In water, above a critical micelle concentration and a critical micelle temperature, the block copolymers form spherical micelles with a PPO core and a PEO corona (7-10 nm in hydrodynamic radius). Furthermore, for micelles of P123, a sphere-to-rod transition at the elevated temperatures has been reported [1]. The size of the NaGDC micelle is 1.6 nm [2]. In mixed NaGDC/copolymer solutions, at low bile salt concentrations, copolymer-rich mixed complexes are formed that become increasingly charged as the concentration of bile salt increases. The electrostatic interaction between the complexes is evidenced in the scattering experiments. At high bile salt concentrations, as the disintegration of the block copolymer micelle begins, bile-salt-rich mixed complexes coexist with the polymer-rich complexes. In addition, the shape change of the P123 micelle is prohibited by addition of the bile salt.

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**Oral Presentations**  
**Tuesday, September 9, 2014**

**New Insight into an Old Puzzle - The Hofmeister Effect Revisited with AFM**

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Extensive measurements of the force acting between two approaching silica surfaces in solution as a function of pH, salt type, and salt concentration provide new insight into the way surface hydration governs specific cation adsorption to the surface and consequently affect surface charging and surface-surface interaction. The results disclose that cation adsorption to the surface is determined by the relative strength of bulk water hydrogen bonds compared with surface-water hydrogen bonds.

At low pH, when the former are stronger than the latter, excess adsorption of chaotropic cations (normal Hofmeister series) takes place, leading to surface neutralization at intermediate salt concentrations and surface charge reversal at higher salt concentrations. At high pH, surface deprotonation leads to the formation of a tight hydration layer that repels chaotropic ions from the surface and leads to the reversal of the Hofmeister series. The normal Hofmeister effect is hence traced by our experiments to hydrophobic expulsion of chaotropes from solution to weakly hydrated surfaces while the reverse Hofmeister order is associated with strongly hydrated surfaces. These findings account for all the experimental data known to us, including overcharging by excess adsorption of chaotropic cations (previously unexplained), the opposite Hofmeister order in high and low pzc oxides, and the reorientation of interfacial water molecules as a function of pH.

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***Invited Lecture:***

**Transition from Surfactant-Free to Surfactant-Rich Micelles and Salt Effects Herein**

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Stjepan Marcelja<sup>3</sup>, Stephane Pellet-Rostaing<sup>2</sup>, Thomas Zemb<sup>2</sup>,  
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Recently, we could prove experimentally that surfactant-free microemulsions (SFMs) do exist. They occur when two immiscible liquids are mixed with a third component that is miscible with both of these liquids. We call this phenomenon "the pre-Ouzo effect", because it occurs in Ouzo-like mixtures, but in the phase region, where the mixture is still monophasic. In the case of water-oil-co-solvent mixtures we can explain and even predict the appearance of micellar-like dynamical aggregates by the balance of hydration forces and entropy, in agreement with scattering results.

When surfactants are added to these initially water-oil-co-solvent mixtures, first all structures and aggregates are destroyed. So surfactants have a destructuring effect on SFMs. Only at significantly high surfactant concentrations classical microemulsions are formed again.

In both cases, classical surfactant-based microemulsions and SFMs, the addition of salts has a significant effect. Depending on the cosmotropic or chaotropic nature of the salts, SFMs can be significantly strengthened in their structure or the structure can be destroyed. If the ions of the salt are of very different hydrophobicity/hydrophilicity the salt alone may even play the role of surfactants, a phenomenon that we call the Onuki effect.

As will be shown with the help of phase diagrams and X-ray scattering results, there can be a continuous cross-over between SFMs, classical surfactant-based microemulsions and "Onuki" microemulsions.

We can conclude that classical microemulsions are only a part of a much more general aggregation phenomenon and, in parallel, that DLVO is only a special case of a much more general theory.

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## **Enthalpic Depletion Forces in Complex Solutions**

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Solutes preferentially excluded from macromolecules can drive depletion attractions in important biological association processes. The established Asakura-Oosawa theory relates depletion forces to the excluded volume reduction and the ensuing entropy gain upon macromolecular compaction. Accordingly, cosolute-induced protein stabilization is often described in terms of entropically driven "crowding". In agreement, our experiments of peptide folding suggest that depletion forces are predominantly entropic for some cosolutes, such as polyethylene glycol polymers. However, for other cosolutes, such as polyol osmolytes, the effect is enthalpically dominated, while the entropic change can even be unfavorable. We show these properties persist for other proteins and macromolecular processes. To elucidate the molecular basis of these depletion interactions, we use simulations and analytic theory. Monte-Carlo simulations follow the association of two rod "macromolecules" in binary Lennard-Jones solutions. By dissecting the association free energy change into the respective thermodynamic components, we find different cosolutes induce stabilization through different thermodynamic driving mechanisms. Even for these simple liquids, considering intermolecular interactions beyond hard-cores can result in depletion forces that are completely enthalpic. We discuss how this newly resolved mechanism originates from intermolecular interactions and solvent restructuring. Finally, a mean-field theoretical model based on the Flory-Huggins solution theory complements the simulation analysis.

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### **Ion Specific Effects: A Possible Way to Reconcile Two Opposing Approaches**

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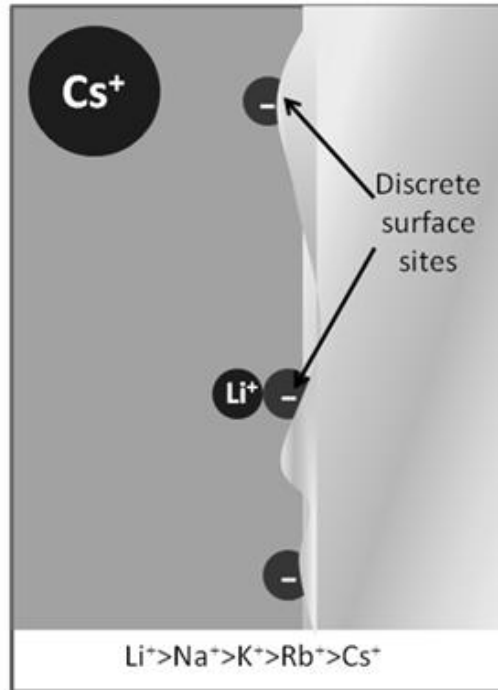
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Ion specificity has posed a challenge since the 1880's according to the pioneering work of Franz Hofmeister on salt induced protein precipitation [1]. These phenomena are ubiquitous both in chemistry and biology [2]. Conventional electrostatic theories (i.e. Debye-Huckel, DLVO) cannot explain such effects. Over the past decades it has been recognised that additional quantum mechanical dispersion forces acting on ions are missing from theory [3]. On the other hand, a phenomenological set of rules known as the *law of matching water affinities* (LMWA), has been proposed [4]. LMWA explains and predicts at a qualitative level the order of ion-ion and ion-surface site interactions. Ion dispersion forces and LMWA approaches appeared to conflict.

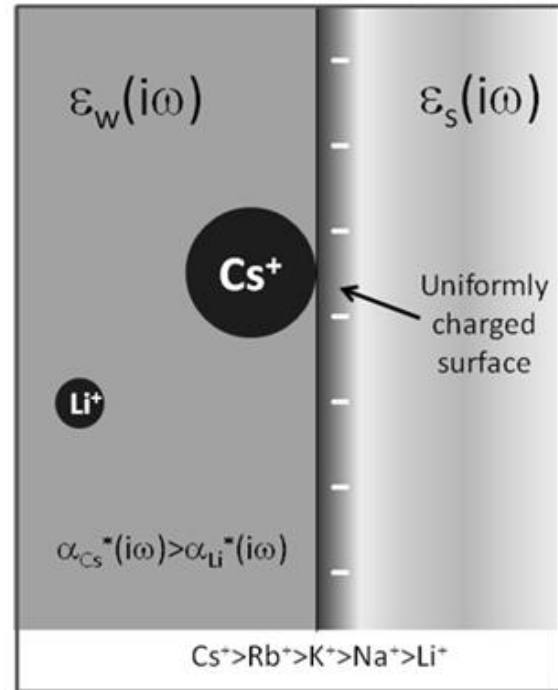
Although the need of inclusion of quantum dispersion forces is not questioned, the modeling used has sometimes not properly described the chemical nature (kosmotropic/chaotropic) of the interacting species. The success of LMWA lies in the fact that it does. Recent experimental results require that both approaches, represented in the figure, are considered depending on the particular system under investigation [5]. Here we show the way that the two apparently opposing approaches could be reconciled.

**A: the law of matching water affinities**



$$\Delta H_{\text{hydr. anion}^-} - \Delta H_{\text{hydr. cation}^+} \approx 0$$

**B: the theory of ion dispersion forces**



$$U_{\text{disp}}(x) = \frac{kT}{2x^3} \sum_{n=0}^{\infty} \frac{\alpha^*(i\omega_n) [\epsilon_w(i\omega_n) - \epsilon_s(i\omega_n)]}{\epsilon_w(i\omega_n) [\epsilon_w(i\omega_n) + \epsilon_s(i\omega_n)]}$$

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## **Surface Tension of Electrolyte Solutions: A Self-Consistent Theory**

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When salts are added in small quantities to an aqueous solution, its surface tension increases due to the dielectric discontinuity at the air/water surface. This idea was implemented in the pioneering work of Onsager and Samaras, who found a universal limiting law for the dependence of the surface tension on the salt concentration. However, the result implies an increase in the surface tension that is independent of the ion type, which turned out to be violated in many physical realizations. Employing field-theoretical methods and considering short-range interactions of anions with the surface, We expand the Helmholtz free energy to first-order in a loop expansion and calculate the excess surface tension. Our approach is self-consistent and yields an analytical prediction that reunites the Onsager-Samaras pioneering result (which does not agree with experimental data), with the ionic specificity of the Hofmeister series. We obtain analytically the surface-tension dependence on the ionic strength, ionic size and ion-surface interaction, and show consequently that the Onsager-Samaras result is consistent with the one-loop correction beyond mean-field. Our theory fits well a wide range of concentrations for different salts using one fit parameter, reproducing the reverse Hofmeister series for anions at the air/water and oil/water interfaces.

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## **Surface Charging and Ion Specific Effects of Protein Modified Air-Water Interfaces**

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The surface chemistry of ions, water molecules and proteins and their ability to form stable networks in foams influences and controls macroscopic properties such as the stability of a macroscopic foam. Despite the importance of protein adsorption at liquid interfaces, a molecular level understanding of proteins and their interactions at aqueous interfaces has been elusive.

Therefore, we address the adsorption of  $\beta$ -lactoglobulin at air-water interfaces with vibrational sum-frequency-generation (SFG) and ellipsometry. SFG provides specific information on composition and average orientation of interfacial molecules, while information on adsorbate thickness is obtained with ellipsometry. Adsorption of charged proteins at aqueous interfaces leads to an electrified interface, pH and ion depending charging and electric field-induced polar ordering of interfacial H<sub>2</sub>O and proteins. Varying bulk pH or ionic strength of protein dilutions changes the intensities of protein vibrational bands substantially, while dramatic changes in OH stretching bands of interfacial H<sub>2</sub>O are simultaneously observed. Furthermore a charge reversal is monitored directly at the interface which helps to tune interfacial properties.

These observations allow us to determine the isoelectric point of  $\beta$ -lactoglobulin at the air-water interface. At a pH near the isoelectric point proteins form an amorphous network of possibly agglomerated proteins, while highly charged proteins form monolayers with strong repulsions. By the addition of salts, protein net charge can be screened and to some extent also varied whereby ionic strength, the nature of cations and thus specific ion adsorption play an important role.

Finally, we provide a direct correlation of the molecular structure of the investigated protein interfaces with foam stability<sup>1,2,3</sup>.

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***Invited Lecture:***

**Reverse Aggregates as Controllable Self-Assembled Systems for Selective Liquid-Liquid Extraction of Multi-Valent Metals by Long Range Interactions**

Thomas Zemb, Sandrine Dourdain, Magalli Duvail, Olivier Diat,  
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Daniel Meyer, Stephane Pellet-Rostaing, Helmut Mohwald  
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In solvent extraction, a concentrated solution of mixed salts is contacted in order to obtain equilibrium with a reverse (w/o) micelle or microemulsion. Desextraction corresponds to the reverse process. Selectivity is obtained via cascades. The common point of all three two-phase equilibrium is that they correspond to a precise point in tie-lines of a pseudo-five component phase diagram.

Selectivity between targeted and non targeted in an efficient separation, due to a difference in chemical potential of the species between the concentrated ionic solution and the reverse micelles: a strong supra-molecular complexation mechanism is in counter-balanced by entropic terms combined in an adsorption isotherm on a divided flexible interface, in order to understand the apparent distribution "constants" and their variation, with formulation and temperature, determination of phase diagram is necessary.

Selectivity between iron and uranium is observed, with up to a factor of 50 increase of the selectivity of extraction. The selectivity is yet an unpredictable effect and depends on the nature of the solvent. The experimental dependence of the solvent is puzzling, since standard "theory" used by engineers does not involve the solvent, but only supra-molecular assembly and competing equilibrium.

We will describe in this talk how the free energy of extraction, i.e. the apparent equilibrium constants depend on the w/o micellisation, i.e. loss of entropy associated to cmc, extractant film bending constant, film extension, image charges and solvent dielectric properties. As a consequence, the selectivity in synergic systems should always show the apparently paradoxical solvent-sensitive peak in selectivity observed and used in applications.

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***Invited Lecture:***

**A General Approach to the Synthesis of Metal Nanoparticles in Dense Microemulsions and Their Application in Fuel Cells**

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Exceptional properties of metal nanoparticles present many opportunities for applications in numerous fields such as catalysis, medicine, electronics, optics. Consequently, much effort has been devoted to the production of nanoparticles in a controlled manner and to increase the production yield in a cost-effective manner. Still, the systematic production of uniform small metal nanoparticles poses a long-standing challenge.

We will report on a general approach for the controlled, high yield synthesis of small and uniform metal nanoparticles in dense microemulsions. Anionic (Na-AOT), cationic (DDAB) and non-ionic (Triton X-100 and Brij-35) were used to produce nanoparticles of different size. By using various types of surfactants, we demonstrate the generality of our approach. It enables us to extend the control over the size, uniformity of nanoparticles and the timescale of the synthesis procedure, compared to the limiting single template system. The approach consists of four crucial steps: (a) selection of a surfactant, (b) study of a phase diagram and selection of suitable microemulsion compositions, (c) synthesis and (d) extraction of the nanoparticles.

As a result metal nanoparticles (such as Pt and Au) with a size range from 2.4 to 6.2 nm were produced. The size and monodispersity was controlled by the surfactant packing parameter. Platinum nanoparticles were harvested on carbon support and tested as a catalyst material in Proton Exchange Membrane Fuel Cell (PEMFC) and showed high activity and excellent durability.

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## **Preparation, Functionalization and Self-Assembly of Janus Dumbbell Nanoparticles**

Marco Lattuada, Florian Guignard  
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In recent years, much attention has been devoted to the synthesis of anisotropic nanoparticles, and in particular of Janus Nanoparticles. In this work, a two-step emulsion based polymerization has been applied to synthesize Janus dumbbell nanoparticles, which size and morphology can be tuned by changing the process parameters. Narrowly distributed polystyrene nanoparticles are used as seeds, covering a wide range of sizes. These seeds are first coated with a random copolymer of styrene and 3-trimethyloxylpropyl acrylate (MPS), bringing silane groups on the surface of the seeds. The particles are then swollen with a monomer solution before a second polymerization. Due to the hydrophilic shell on the surface of the nanoparticles, the newly formed polymer is bulging out of the seeds, giving birth to dumbbell-like nanoparticles. Depending on the amount of swelling, dumbbells with different aspect ratio can be prepared. The resulting nanoparticles are not only anisotropic in shape, but also in surface chemistry. Only the first bulb is bearing silane groups, which can be functionalized by means of silane chemistry. Positively charged groups have been added to the surface of the nanoparticles, so as to create dipolar particles. Several types of negatively charged nanocrystals can be attached to the positively charged bulb of the dumbbells. Superparamagnetic iron oxide nanoparticles (SPIONS) allow the preparation of magnetic hybrid particles, which align into peculiar chain-structures depending on their size and aspect-ratio. The same approach has been used for platinum nanocrystals, leading to particles that can be used as Janus nanomotors in  $H_2O_2$  solution. Additionally, silica shell can be grown on top of the silane functionalized bulb, followed by polymer removal, finally leading to silica nanobowls.

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**Electrical Field Induced Charging of Single Colloidal Particles**

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In combination with optical tweezers, electrophoresis allows for accurate charge monitoring of single particles over long time intervals. The potential of this technique has been demonstrated by Beunis et al. [1], by measuring changes of only one elementary charge on a colloidal particle. This technique opens the possibility to study the dynamics of particle charging processes in e.g. nonpolar liquids, which are not yet understood. A PMMA particle with a radius of 500 nm in n-dodecane is optically trapped between two parallel transparent electrodes, and is subjected to an AC electric field. The oscillating field induces a sinusoidal particle movement, which is monitored by analyzing the scattered laser light measured with a quadrant photodiode. Under these conditions, the surface charge of the particle can be measured accurately enough to distinguish single electron charges. We find that the charge increases over time as a result of the applied electric field, until it saturates at a surface charge value which is an order of magnitude higher than the initial charge.

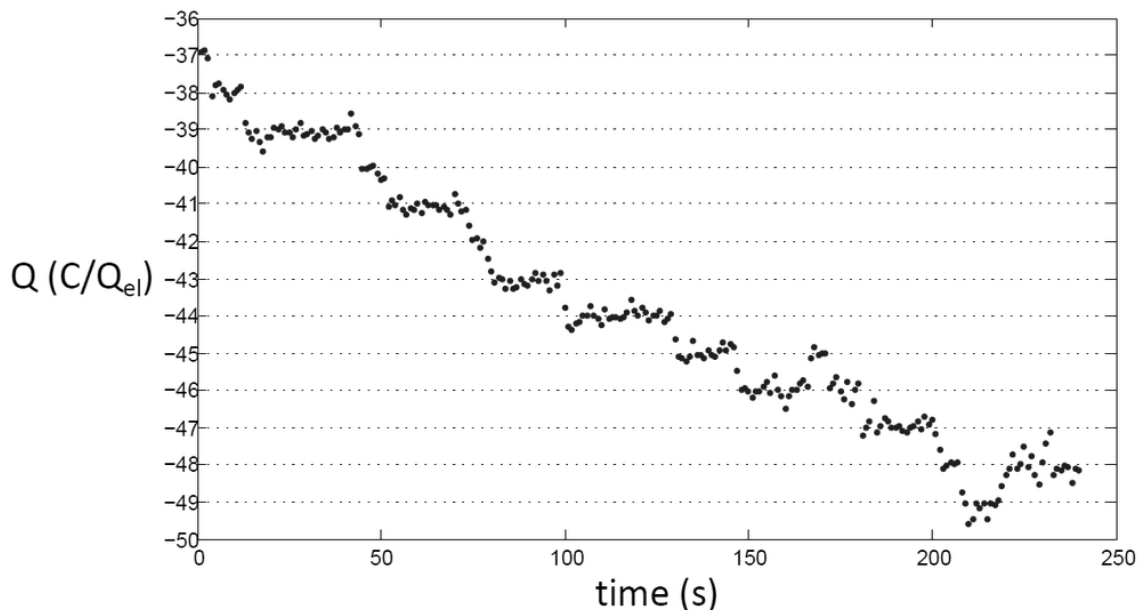


Fig. 1. Measurement of the charge  $Q$  divided by  $Q_{el} = 1,714 \cdot 10^{-19} \text{C}$ , which is the periodicity in the charge histogram corresponding to the elementary charge.

Acknowledgements:

We thank the agency for Innovation by Science and Technology (IWT), the IAP-VI project photon@be funded by BELSPO, the Belgian Science Policy program and the Hercules Foundation (project AUGE/013).

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**Nano-Segregated Polymeric Domains on the Surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Particles**

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Diego Mendez Gonzalez<sup>1</sup>, Marco Laurenti<sup>2</sup>, Raul Olivero-Ruiz<sup>1</sup>,  
Jorge Rubio-Retama<sup>1</sup>

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Multifunctional, biocompatible and brush-grafted poly(ethylene glycol)/poly( $\epsilon$ -caprolactone) (PEG/PCL) nanoparticles have been synthesized, characterized, and used as vehicles for transporting hydrophobic substances in water. For anchoring the polymer mixed brushes, we used magnetic-silica particles of 40 nm diameter produced by the reverse micro-emulsion method. The surface of the silica particle was functionalized with biocompatible polymer brushes, which were synthesized by the combination of "grafting to" and "grafting from" techniques. Poly(ethylene glycol) was immobilized on the particles surface, by "grafting to", whereas poly( $\epsilon$ -caprolactone) was growth by ROP using the "grafting from" approach. By varying the synthetic conditions, it was possible to control the amount of PCL anchored on the surface of the nanoparticles and consequently the PEG/PCL ratio, which is a vital parameter connected with the arrangement of the polymer brushes as well as the hydrophobic/hydrophilic balance of the particles. Thus, adjusting the PEG/PCL ratio, it was possible to obtain a system formed by PEG and PCL chains grafted on the particle's surface that collapsed in segregated domains depending on the solvent used. For instance, the nanoparticles are colloidally stable in water due to the PEG domains and at the same time are able to transport, entrapped within the PCL portion, highly water-insoluble drugs.

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## **Understanding of Structural and Physical Properties of Thermoresponsive Copolymer Microgels Based on Alkylacrylamides Exhibiting Consimilar Structures**

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Temperature responsive microgels undergo a volume phase transition at a certain temperature. Such kind of materials are interesting for various applications, such as drug delivery systems or in catalysis. An optimal performance of microgels requires a method for an adjustment of the application-specific properties. Especially the particle size and the volume phase transition temperature (VPTT) are a matter of particular interest.

In this study we present experimental results regarding the influence of the feed composition, the chemical structure of the incorporated monomers and the amount of surfactant in the synthesis procedure on the properties of copolymer microgels. Therefore, we prepared microgels based on two of the following temperature responsive alkylacrylamides in the presence of different surfactant amounts under equal reaction conditions. The used monomers are *N*-*n*-propylacrylamide (NNPAM), *N*-isopropylacrylamide (NIPAM) and *N*-isopropylmethacrylamide (NIPMAM) with VPTTs of 22°C, 32°C and 43°C, respectively. For the characterization scanning electron microscopy, dynamic light scattering, small angle neutron scattering, light attenuation measurements and pyrene probe fluorescence measurements were used.

All monomer combinations and feed compositions yielded spherically shaped particles exhibiting a low polydispersity. Adding surfactant in the synthesis reduces the particle size, whereby the strength of the effect is depending on the monomer structure. Interestingly, a linear correlation between size and composition is observed for all systems synthesized in presence of surfactant and the limits of the microgel dimensions are predetermined by the homopolymer systems. Because of that, a precise tuning of the particle size is achievable. Additionally, the VPTT depends also linearly on the composition and this interdependence is not affected by the surfactant. Due to that, a simultaneous tuning of the particle size and the VPTT is possible, which constitutes an important result concerning the usage of microgels for various applications.

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***Invited Lecture:***

**Aggregation and Stability of Polyelectrolyte-Decorated Liposome Complexes in Water-Salt Media: The Effect of Surface Charge Density**

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Recently, there has been a renewed interest in the study of the mechanisms governing the complexation of polyelectrolytes and oppositely charged colloidal particles, due to the still not completely understood aggregation phenomenology and to the increased awareness of their potential for innovative applications in nano-medicine and nano-biotechnology [1]. Despite the initial disparity of the early results that appeared in the literature, due to the variety of the experimental conditions and to the intrinsic complexity of these systems, the interesting phenomenology can now be described within a unified picture [2] where electrostatic interactions are the main driving force of the cluster formation, and the non-uniformity of charge distribution, resulting from the correlated adsorption of the polyelectrolyte on the colloid surface, plays a pivotal role. However, there is still a lack of a complete theory able to describe satisfactorily all the different features of the observed complexity. To clarify this point, we begin to explore systematically the phase diagram of a typical polyelectrolyte/colloid system, considering in addition to the effects of the polyelectrolyte/colloid charge ratio and temperature, also those of the ionic strength of the aqueous suspending medium. We show that a simple interparticle potential built up as the sum of two terms is able to account for the observed phase diagram very satisfactorily [3]. Now we consider the effect on the phase diagram of the surface charge density on the colloidal particles and show how the salt addition modifies the phase diagram promoting the cluster dissolution due to a polyion desorption, as predicted by theoretical models [4].

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## **Line Active Hybrid Lipids Promote the Formation of Nanoscale Domains in Model Membranes**

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A ternary mixture model is proposed to describe the phase behavior of model membranes composed of saturated, unsaturated and line active hybrid lipids. In particular, the formation and the stability of nanoscale domains, motivated by the presence of lipid rafts in cells, are studied. The asymmetric hybrid lipid (with one saturated and one unsaturated chain) can reduce the packing incompatibility between domains of saturated and unsaturated lipids by residing at their boundary. The model predicts the nanostructure and phase behavior by taking into account the dependence of the interactions of the hybrid lipids on their orientations in a simple manner. In the single phase, mixed regime, the theory predicts correlation lengths and correlation times that are, respectively, shorter and longer when hybrid lipids are added. Nanoscale fluctuation domains similar to lipid rafts are more probable and have longer lifetimes than in two-component, saturated/unsaturated mixtures. In the phase separated (coexistence) regime, zero line tension between domains rich in saturated/unsaturated lipids is predicted to occur at physiologically relevant temperatures and large hybrid fractions. Under these conditions, the membrane can spontaneously form more interfaces and promote the formation of stable nanoscale domains.

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## **Salt-induced Detachment of Non-touching Colloidal Particles from Oil-water Interfaces**

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Solid particle stabilized emulsions (Pickering emulsions) provide interesting opportunities for the stabilization of liquid-liquid interfaces, for self-assembly on liquid interfaces and for the formation of colloidosomes. Besides, particles strongly adsorbed at a 2D interface are an important realization of a 2D model system in a 3D world. In various studies, it has already been reported that the physics in 2D, including the interparticle interactions and the phase transitions, is fundamentally different from 1D and 3D. What all interfacial studies performed so far have in common, is that the particles interpenetrate the oil-water interface as the colloids are wetted both by oil and water. Addition of salt to one of the phases can result in 2D (in plane) melting of a colloidal solid in these systems. In this presentation, we will discuss a surprising, new result: our particles could be detached from the interface by addition of salt only. Our results therefore indicate that the particles are not irreversibly trapped at the interface and hence this suggests that particles are non-touching, meaning that they are completely immersed in the oil phase. In principle, the entrapment of non-touching colloids near an oil-water interface could be theoretically explained by a balance between image charge attractions [1,2] and Van der Waals repulsions [3]. In this presentation, we will discuss these new experimental findings and describe the above discussed salt-effects.

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### **Polymer Brushes from a Novel Polymer Initiator**

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Polymer brushes can readily modify interfacial properties such as anti-fouling, frictional and wetting properties. Grafting polymer brushes from surfaces is commonly achieved by using Atom Transfer Radical Polymerisation (ATRP), for which a key step is to pre-initiate (i.e. functionalise) the surface with halogen groups, often *via* a covalently bound silane initiator. A promising alternative route to surface initiation is to utilise a polyelectrolyte molecule to anchor the initiation groups to the surface, achieved by a simple dip-coating technique.<sup>1,2</sup>

In this work we have designed and synthesised a novel two dimensional (2D) polyelectrolyte 'mat' initiator molecule with its networked structure bearing both cationic and halogen groups. The advantage of this approach lies in the tunability of the ratio of anchoring to initiation sites, *via* the degree of branching and crosslinking in the polymer mat architecture and its overall molecular weight to tailor both the polymer mat size and activity. This facilitates direct influence over the surface anchorage of polymer brushes subsequently grown and the brush grafting density.

Using these novel 2D mat initiators, we have grafted a number of different polymer brushes from both mica and silica, containing monomers of amino acid, 2-(dimethylamino)ethyl methacrylate and polyethylene glycol. Our AFM, ellipsometry and X-ray reflectivity results indicate that the grafted polymer brushes possess high surface coverage and low surface roughness on the nanometre scale. We suggest that this 2D mat initiator provides a novel and versatile route to grafting a variety of polymers to essentially all surfaces, useful both for polymer brush applications and academic research.

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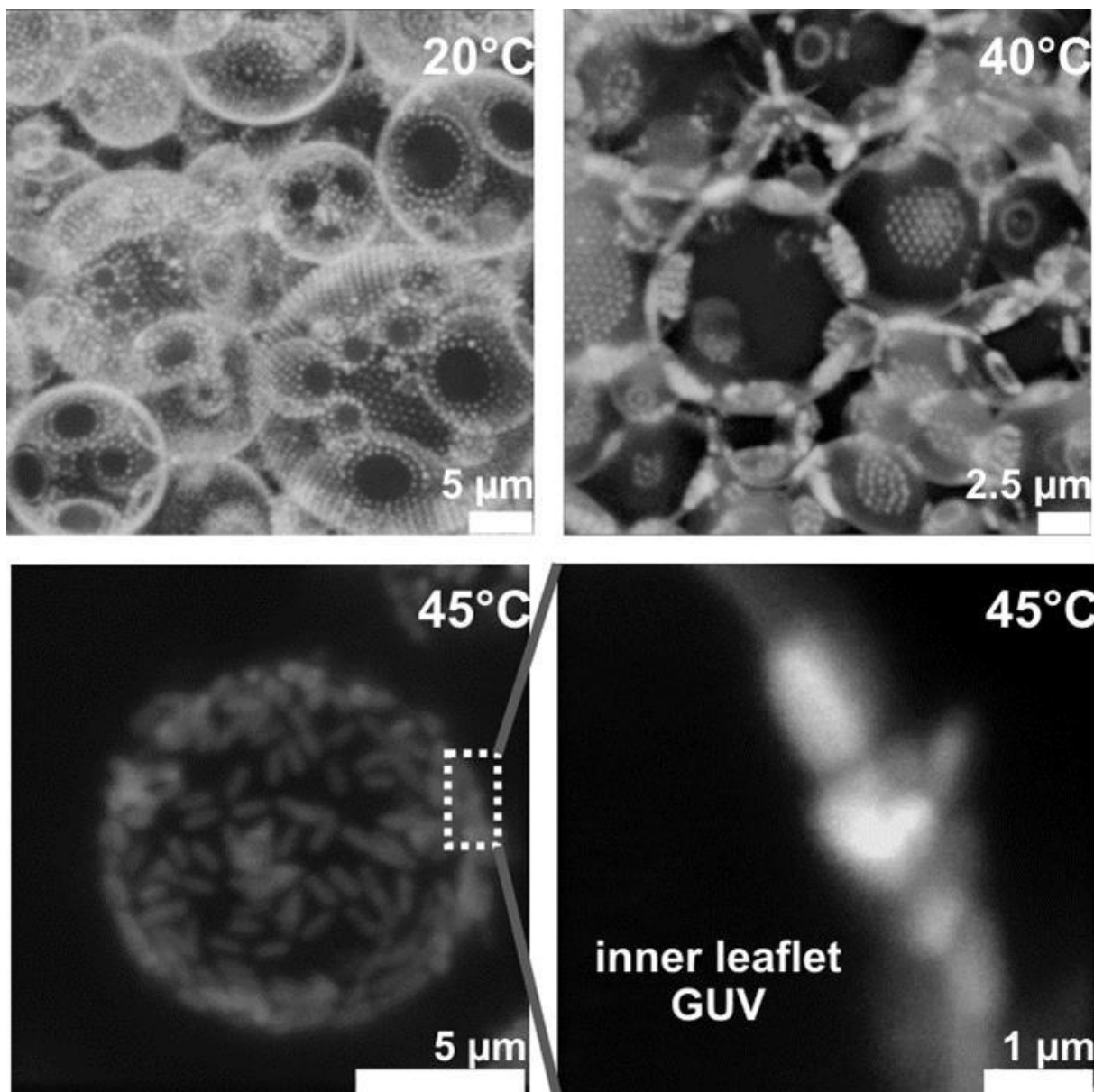
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### **Tunable Adsorption of Soft Colloids on Model Biomembranes**

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We investigate the interactions of responsive microgel particles with lipid biomembranes. These particles feature a rapid volume phase transition close to human body temperature and have the ability to adapt both their conformation and interaction potential to the local environment. Spherical PNIPAM microgels are acting as switchable stabilizers for giant unilamellar vesicles (GUVs).<sup>1</sup> These particles can be used to increase and control the stability of lipid vesicles where their softness and deformability play a major role. At 20°C, the swollen and hydrophilic microgels adsorb evenly and densely pack in 2D hexagonal arrays at the DOPC GUV surfaces, whereas above their volume phase transition temperature ( $T_{VPT}=32^{\circ}\text{C}$ ), the collapsed and more hydrophobic particles partially desorb and self-organize into domains at the GUV/GUV interfaces. Furthermore, the shape anisotropy and initial orientation of the particles are crucial to the interactions between the particle and the lipid bilayer, where the penetrating capability of a nanoparticle is influenced by the contact area with the membrane and the local curvature of the particle at the contact point.<sup>2</sup> Unlike spherical microgels, core-shell ellipsoidal PNIPMAM-PS composite microgel not only facilitate a higher adhesion due to the large surface contact area on the GUV surface, but at their volume phase transition (45°C) can facilitate penetration across the lipid bilayer that is determined by a larger local curvature of the particle at the contact point.



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## **Dynamics of Bubble Adhesion Under Presence of Different Surface-active Agents**

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Knowledge of bubble-particle interaction is important in many industrial processes such as in flotation. While the collision (first interaction sub-process) between bubbles and particles is influenced only by hydrodynamic forces, the bubble behaviour during the attachment (second sub-process) is influenced both by hydrodynamic and surface forces. This work is focused on the study of the three-phase contact (TPC) line expansion during bubble adhesion on hydrophobic surface and on its experimental and mathematical description. The experiments were carried out in aqueous solutions of surface active agents. Influence of different type and size of surfactants (anionic SDS, cationic DTAB, non-ionic Triton and Terpineol) was compared with data obtained for pure water. The attachment process was recorded using a high-speed digital camera and diameter of TPC line as well as the dynamic contact angle were determined. Altogether the dynamic surface tension was measured. The molecular-kinetic model was used for mathematical description of the TPC line expansion.

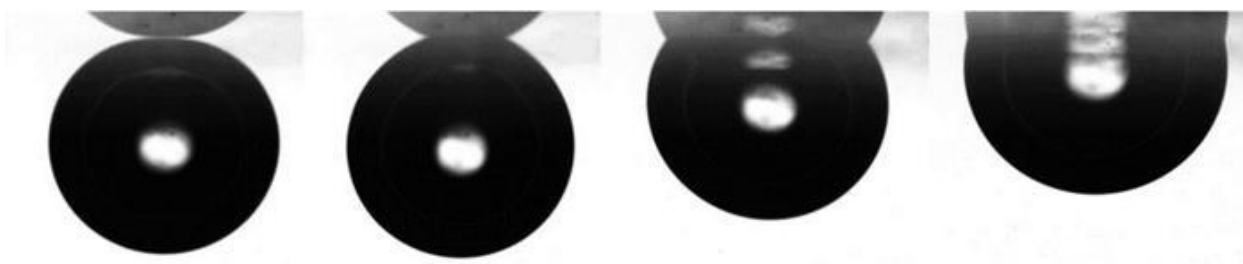


Fig. 1 Bubble adhesion onto the hydrophobic solid surface

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## **Linear and Nonlinear Rheology of Dense Emulsions Across the Glass and the Jamming Regimes**

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We discuss the linear and nonlinear rheology of concentrated silicone oil-in-water emulsions, amorphous disordered solids composed of repulsive and deformable soft colloidal spheres. Based on recent results from simulation and theory, we derive quantitative predictions for the dependences of the elastic shear modulus and the yield stress on the effective droplet volume fraction [1]. The remarkable agreement with experiments we observe supports the scenario that the repulsive glass and the jammed state can be clearly identified in the rheology of soft spheres at finite temperature while crossing continuously from a liquid to a highly compressed yet disordered solid. For emulsions of nanoscale droplets, known as nanoemulsions, however, the radius begins to approach the Debye screening length and these systems can become elastic solids at very low droplet volume fractions, even as low as about twenty percent. For this case the concept of an effective volume fraction cannot properly account for the electrostatic repulsions. To address the rheology of nanoemulsions we combine the interaction potential associated with droplet jamming and deformation with a full treatment of the screened charge repulsion between charged droplets [2]. Finally we show that the onset of elasticity due to entropic contribution can be described by a quasi-equilibrium analytical model of linear elasticity that includes energetic contributions from entropy and soft interfacial deformation [3]. The comparison of the comprehensive, yet simple, models with experimental data demonstrates the possibility to describe the rheology of a wide range of charge-stabilized emulsions having droplet sizes ranging from the macroscale to the nanoscale.

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## Catanionic Gels Based on Cholic Acid Derivatives

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Supramolecular gels are widely studied for their interest in many applications ranging from food, cosmetic thickeners, and textile fibers to support matrices for drug delivery and tissue replacement. In recent years many works have been published aimed at investigating the fundamental aggregate structures in the gels and the intermolecular interactions stabilizing them which turns out to be extremely important for the applications. As reported in many published results, pure bile salts and cationic analogues have generally remarkable gelling properties. Starting from this knowledge, anionic and cationic derivatives containing aromatic moieties were synthesized in order to enhance their gelling ability by the formation of  $\pi$ - $\pi$  stacking. In addition catanionic mixtures were prepared to exploit the effect of electrostatic attraction in the gel formation [1]. The results show that only the cationic derivative form gels as a pure surfactant solution. However the presence of favorable electrostatic interactions allows to get more efficient gels in catanionic mixtures both in terms of mechanical properties and minimum gelation concentration. Compact gels with total surfactant concentration of 0,05% w/v were obtained. Therefore this work suggests that catanionic mixtures can be used to enhance the gelator efficiency of molecules, constituting an information of quite general importance in the preparation of molecular gels. Moreover, beside the high gelation efficiency, these catanionic mixtures could also provide gels of fibrils with tunable charge, which could allow the regulation of their interaction with cells or active molecules and macromolecules, further widening their applicative range.

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## Surfactant Adsorption and the Equation of State, Obtained from Kinetic Interfacial Tension Data

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We discuss a procedure for interpretation of experimental results for dynamic interfacial tension, at O/W or A/W boundaries. Based on a previous theory [T. Gurkov, *Colloid Polym. Sci.* 289 (2011) 1905], data points for the surface pressure  $\Pi$ , measured vs. time and at different surfactant concentrations, can be represented in the form of a "master curve". The latter is fitted with an appropriate surface equation of state, which takes into account the lateral interactions and the sizes of surfactant and solvent molecules [T. Gurkov et al., *Colloids Surf. A* 87 (1994) 81]. This method is applicable at  $\Pi$  smaller than about 18, 14, or 9 mN/m depending on the system. The good agreement between theory and experiment allows one to quantify the adsorbed amount per unit area, and its time evolution,  $\Gamma(t)$ . The interaction parameter ( $\beta$ ) in the equation of state is also determined. For the anionic surfactant Na-laurate at A/W interface, the electrostatic contribution to  $\Pi$  is included; the results for  $\Gamma(t)$  reveal a barrier mechanism for adsorption, with the characteristic time of  $\sim 150$  min. In addition,  $\beta=6.5$ , which indicates a significant lateral attraction. The cationic surfactant cetyl trimethylammonium bromide on hexadecane/water boundary, in the presence of salt, shows  $\beta=0$  and diffusion-controlled adsorption, possibly affected by pre-micellar aggregates. For the non-ionic surfactant C<sub>10</sub>EO<sub>4</sub> at A/W, the analysis of literature data demonstrates purely diffusional mechanism of adsorption. Interesting is the fact that  $\beta=-8.9$ ; the observed repulsion of considerable magnitude is probably due to the extending polar headgroups. Our calculations can be useful for analysis of measured data for adsorption dynamics in undersaturated surfactant layers (at degree of coverage below  $\sim 0.5-0.6$ ).

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## **The Influence of Reduced Graphene Oxide and Conductive Polymers on the Electrocatalytic Properties of Multilayer Films Containing Prussian Blue Nanoparticles**

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Prussian blue (PB) shows high activity and selectivity toward the reduction and oxidation of hydrogen peroxide. It has been extensively studied for the construction of electrochemical sensors and biosensors, in particular for measuring hydrogen peroxide concentration.

PB nanoparticles were immobilized in polyelectrolyte (PE) multilayers using the layer-by-layer method. Graphene oxide (GO) was deposited from its aqueous suspension forming additional layers of the film. Then the multilayers films were exposed to the elevated temperature, 180°C, to turn graphene oxide into its reduced form (rGO). We compared, using the cyclic voltamperometry, the electroactive and electrocatalytic properties of PE/PB multilayer films with ones containing rGO or conductive polyelectrolytes: poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), polypyrrole and polyaniline. The incorporation of the conductive polymers enhanced the electroactive properties of PE/PB multilayer films by up to 100%, which could be associated with more effective deposition of PB nanoparticles in films with some conductive polyelectrolytes as well enhancement of electron transfer to the electrode surface. On the other hand the multilayers with the reduced graphene oxide showed up to 40 times higher PB redox current densities than films constructed only with nanoparticles and polycation - poly(allylamine hydrochloride) (PAH). Due to synergistic, electrocatalytic effect for the redox processes of hydrogen peroxide and enhanced conductivity of rGO, the electrodes covered with hybrid (PB/PAH/rGO) films showed high current densities in the micro- to milimolar solutions of H<sub>2</sub>O<sub>2</sub>. That indicates on the possibility of the application of those films as effective sensor layers for the electrochemical detection of hydrogen peroxide.

### Acknowledgments:

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## Can we Describe Protein Adsorption in Terms of Electrostatic Interactions?

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Protein adsorption at solid-liquid interfaces is an important issue in many fields such as: bio- and hemocompatible materials, diagnostic kits or enzymatic activity in mineral soils. The theoretical description of the protein adsorption phenomena is very complicated due to combination of many types of interactions involved as: electrostatic, dispersive, hydrophobic/hydrophilic, specific ion effects. Just considering only the electrostatic interactions with solid surface we need to take into account that the surface charge of proteins is pH dependent and non-uniformly distributed. The concept of non-uniform charge distribution is usually used to explain anomalous adsorption of proteins at the charged surfaces carrying the surface charge of the same sign as the mean charge of protein. For example human serum albumin (HAS), which above pH 5 has net negative charge and can be deposited at mica surface [1], whereas casein can be deposited on silica surface in the broad pH value regardless that it has isoelectric point around pH 5.

We used molecular modeling calculation to determine the distribution of the surface charge at the selected proteins ( $\alpha$ -chymotrypsin,  $\alpha$ - and  $\beta$ -casein, HSA). The modeling was conducted in Accelrys Discovery Studio 3.5 package using CHARMM force field. The enzyme's pI was calculated with 'Calculate Protein Ionization and Residue pK' protocol and the protein net charge and its electric dipole moment was estimated for pH conditions at, below, and above pI point. We compared the dependencies of the net charge of proteins on pH obtained from the calculation with ones measured experimentally by the microelectrophoresis. Then, we evaluated the electrostatic interactions between proteins having nonuniform distribution of surface charge with uniformly charged, planar interface. The interaction force exerted on the particle were calculated by solving numerically three dimensional nonlinear Poisson-Boltzmann equation. The interaction energy was calculated by integration of the force distance relationship. These theoretical predictions were used for the interpretation of experimental data [1-4] for the adsorption and desorption kinetics of proteins at mica surface.

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**Surface Energetics Evolution During Processing of Biomass-Based Furan Composite**

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Biocomposites made of natural fibers and biomass-based thermoset resins aim at playing a significant role in the fields of construction, automotive, and aeronautics thanks to their light weight property and absence of petro-chemical origins. Furan resin, produced from the hemicellulosic part of agricultural wastes, reinforced by flax fibers is a promising biocomposite as it should combine the intrinsic good mechanical properties of the natural fibers with the excellent fire performance of the bio-based resin. The interfacial strength between the fibers and the resin also determines to a large extent the final properties of the materials, i.e. the compatibility between both constituents must be good to guarantee an homogeneous impregnation of the fibers. To predict such compatibility, surface energetic components of the fiber and the cured resin are traditionally assessed and compared. However, such method is subjected to criticism as during the processing of the composite, the resin, in liquid and not in solid state, first impregnates the fibers and only later on cures. As the chemical nature of the resin is modified during curing, different surface energetic components between the uncured and cured resins are expected. This hypothesis was checked for a furan water-based resin which shows a modification of its Lifshitz-Van der Waals component as well as its acidic and basic components. This work demonstrates the need for a better characterization of reactive resins in order to provide a more reliable prediction of their compatibility with fibers which should eventually lead to better biocomposites.

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## **Diffusion of Functionalized Silica Nanoparticles in Liquid Viscous Media and Permeation into Biological Tissues**

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Sub-100 nm thiolated silica nanoparticles were synthesized by self-condensation of (3-mercaptopropyl)trimethoxysilane (MPTS) in dimethylsulfoxide [1]. These nanoparticles offered an excellent platform for further functionalization such as fluorescent labelling and covalent attachment of hydrophilic polymers (polyethyleneglycol, poly(N-isopropylacrylamide) and poly(2-ethyl-2-oxazoline)) [2]. The thiolated and functionalized nanoparticles were characterized using a range of physicochemical methods including dynamic light scattering, nanoparticle tracking analysis, small angle neutron scattering and transmission electron microscopy. The thiolated nanoparticles were found to exhibit excellent adhesion to biological surfaces such as ocular and urinary bladder mucosa, which makes them promising for development as drug delivery systems. They also were found to be an excellent model to probe the barrier function of ocular membranes. The diffusion of fluorescently labelled thiolated and PEGylated nanoparticles in solutions of different water-soluble polymers was studied using nanoparticle tracking analysis (NanoSight Ltd) [3]. It was established that the diffusivity of nanoparticles is not only affected by their dimensions and solution viscosity, but also by the specific interactions with the components of the liquid media. The nanoparticles functionalized with polymers were found to exhibit enhanced diffusion in biological media such as mucus gels.

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## **Structural and Thermodynamical Properties of Intrinsically Disordered Proteins: a Combined Theoretical and Experimental Study**

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The existence of functional disordered (unstructured) proteins has been recognized for many years, and unstructured proteins were observed in intact cells in early proton NMR experiments. About 10% of all proteins are fully disordered and about 40% of eukaryotic proteins have at least one long disordered region. However, due to the classical structure-function paradigm, the functional role of intrinsically disordered proteins (IDP) has only recently been recognized. Biochemical evidence has since shown that these proteins are functional, and that the lack of a folded structure is related to their function. These proteins can also be found in saliva, where they play an important role in oral health, but also in milk products.

We would like to present results from a combined experimental and theoretical study, where the aim is to develop a model for flexible proteins and to relate the lack of structure of the proteins in solution with their function and structure when adsorbed to surfaces. For this purpose, we are combining atomistic and coarse-grained modelling, with simulation techniques such as molecular dynamics and Monte Carlo simulations. The bulk properties of proteins are studied by osmometry and DLS/SAXS, whereas surface adsorption properties are studied by ellipsometry. Statistical thermodynamics and polymer theory serves as a base for the model development.

As model proteins we are using one short cationic peptide (Histatin 5) and one longer anionic protein with amphiphilic character ( $\alpha$ -casein). Hence, thereby we are covering many different aspects of protein properties that can be found. For example, at physiological pH Histatin 5 is basic and has a positive charge, and due to its richness in histidins it has a high charge capacitance whereas  $\alpha$ -casein is a self-associating proline-rich phosphoprotein, with an amphiphilic character at neutral pH.

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## **Physical-Chemical Investigation of New Cationic Lipids for Gene Transfection**

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The gene-therapy could be a promising way to cure human diseases like AIDS, cystic fibrosis or cancer. Therefore, cationic lipids were developed as a DNA carrier to create the so-called lipoplexes. The lipoplex should be able to cross the cell membranes and release the DNA near the cell nucleus. The delivery is depended on the structure of these complexes (cationic lipid and negatively charged DNA). For this reason new cationic lipids are permanently synthesized, and their physical-chemical properties have been characterized in 2D (monolayers at the liquid/air interface) and 3D (aqueous dispersions) [1]. To determine the properties of 2D monolayers, we use the pressure/area isotherms, infrared reflection absorption spectroscopy and x-ray methods like GIXD, Reflectivity and TRXF. For experiments in bulk SAXS and WAXS have been used.

The various lipids have a similar basic structure in which the chain pattern differs by the unsaturation degree. Additionally, various head groups with different number of amine groups have been used.

The increasing fluidity (double bonds in the chains) and the increasing size and charge of the head group have an influence on the phase state and the protonation degree of the lipids. We used TRXF to quantify the number of charges per molecule at different pH values. The phase state of the lipid chains has been measured by IRRAS. Furthermore, the adsorption of calf thymus DNA on the lipid monolayers has been quantified by IRRAS depending on the sub phase pH value. The results will be discussed as a function of the chemical structure of the lipids.

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***Invited Lecture:***

**Phase Transformations in Mixtures of Surfactants and Lipids: Thermodynamic, Structural and Kinetic Aspects**

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Detergents are routine tools in biomembranes research, being essential for identification and characterization of solubilized micellar proteins. Yet, solubilization of biomembranes has not been systematically studied because of the complex composition of biomembranes. Therefore, much work has been devoted to solubilization of the relatively simple model membranes known as liposomes. Much data is available on the self-assembly of mixtures of bilayer-forming amphiphiles, particularly phospholipids, and micelle-forming amphiphiles, commonly denoted detergents. Here we review on the thoroughly investigated structure of such mixed assemblies, the theoretically rationalized phase diagrams and their dependence on various factors and the mechanisms of the composition-induced phase transformations between micellar and lamellar structures. The structure of such mixed assemblies is rationalized in terms of the balance between the large spontaneous curvature of the "curvophilic" detergent and the "curvophobic" phospholipids. Specifically, we propose that solubilization is the result of a balance between two parameters: (i) the energy associated with bending of phospholipid monolayers into a curved micellar surface, and (ii) the energy associated with filling the void in the center of the resultant mixed micelle.

We show that reliable data on the phase boundaries, and their dependence on various conditions, are consistent with this hypothesis, even if the data might have been interpreted differently. To explain the mechanism involved in solubilization, we first discuss previous data and ideas regarding this process. An important previous finding is that membrane solubilization by some detergents is relatively slow and that the common attribute of these detergents is that their trans-bilayer movement, commonly denoted "flip flop" is very slow. In other words, only detergents that can "flip" into the inner monolayer cause relatively rapid solubilization. Another important process is that detergents induce size growth of small liposomes, including those formed during solubilization, as well as those formed upon reconstitution of liposomes from mixed micelles.

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**Ionic Liquids as Model Systems for Investigation of Ion Size and Structure on the Micellization Processes in Solutions**

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Recently, it has been shown that small changes, such as different position of the substituent on an aromatic ring in the structure [1,2] and the hydrophobicity of counterions [3] considerably influence the self-assembly process like micellization of ionic surfactants.

This effect has been investigated on cationic surfactant dodecyltrimethylammonium chloride and relatively small number of counterions (pharmaceutically important anion mainly). The problem is that there are no much appropriate anions which differ in the hydrophobicity and can be chosen for further investigation. Therefore ionic liquids can serve excellent model systems because they exist in diverse structure and the hydrophobic part of the cation can be varied broadly.

In this work the influence of imidazolium based ionic liquids on aggregation processes of anionic surfactant sodium dodecylsulfate will be studied by isothermal titration calorimetry giving the data on the thermodynamic parameters of aggregation process (free energy, enthalpy, entropy and heat capacity changes). The relation between the heat capacity change and the hydrophobic effect, affected by the additional hydrophobic surface (from counterion) included into the dehydration process upon micellization, will be discussed.

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## **Ion-Specific Hofmeister Effects in Colloidal Aggregation in Aqueous Solutions of Simple Electrolytes and Ionic Liquids**

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In the present work, aggregation of two oppositely charged hydrophobic colloidal particles (sulphate and amidine functionalized polystyrene latices) were investigated in the presence of simple electrolytes and ionic liquids by electrophoresis and time-resolved dynamic light scattering.

In order to maintain the charge of particles and to avoid disturbing CO<sub>2</sub> absorption, all measurements have been performed at pH 4.0. As for the coagulating agents the anions as well as the cations were varied systematically to study their effects comprehensively. Experiments of four different series such as sodium (Na<sup>+</sup>) and 1-butyl-3-methylimidazolium (BMIM<sup>+</sup>) for the different anions while chloride (Cl<sup>-</sup>) and dicyanamide (DCA<sup>-</sup>) for the different cations have been compared. The results reflect the Hofmeister effect in an excellent way; in case of highly charged sulphate latex particles one can observe a smaller shift in the critical coagulation concentrations when varying the simple electrolytes, while in case of positive particles this effect is more pronounced. Moreover, the constituents of Ionic Liquids (ILs) show interesting behavior. Depending if they act as counterions or co-ions in case of cations specific adsorption can be observed, while varying the anions similarities to simple electrolytes can be seen. The electrophoretic mobility measurements confirm the stability behaviors. Accordingly, screening, neutralization and overcharging but no restabilization can be observed at the concentration range investigated even in the presence of ILs which is in good agreement with previous results [1]. This behavior was found for both particles, hence it can be considered as generic. The results are summarized in an extended Hofmeister series.

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**Application of Humidity Scanning QCM-D for Characterization of Sorption-Desorption Hysteresis in Biopolymers**

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Quartz crystal microbalance with dissipation monitoring can be used to study hydration of biopolymers [1-3]. In humidity-scanning modification of this method, the water activity is set up by a non-saturated solution of lithium chloride, which is continuously diluted during the experiment. Thus, water activities are scanned from low values (close to those of saturated LiCl solutions) to very high values [2]. Here we report a further development of the method that allows performing not only continuous increase but also continuous decrease of humidities in QCM-D experiments. We applied this method to study sorption-desorption hysteresis in three biopolymers: hen egg white lysozyme, porcine gastric mucin (PGM) and bovine submaxillary gland mucin (BSM). The experiments were conducted in films of biopolymers, applied on solid surfaces of QCM-D sensors. All three biopolymers showed pronounced sorption-desorption hysteresis, although the nature of the hysteresis was different in case of lysozyme compared to PGM and BSM. Earlier it was suggested that lysozyme may have two hysteresis loops: one due to the glass transition and the other one due to changes in aggregation of lysozyme molecules [4]. This idea is discussed based on the obtained QCM-D data using results of Raman studies of hydration of lysozyme [5].

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## Breaking the Symmetry of Ions at the Air Water Interface

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The classical textbook picture of electrolytes at the air-water interface is shaped by surface tension measurements. Usually ions increase the surface tension, which is then interpreted within the framework of Gibbs Thermodynamic as a zone of depletion. This picture was challenged in the last decade by mounting evidence that ions may reside at the interface and moreover adopt a non-monotonous concentration profile.

In this contribution we investigate the large and easy polarisable ion hexacyanoferrate  $[\text{Fe}(\text{CN})_6]^{4-}$  by IR-VIS sum frequency generation (SFG) spectroscopy and surface tension measurements. The equilibrium surface tension increases in a monotonic fashion with the bulk concentration. Due to selection rules a prerequisite for a second order nonlinear response is the simultaneous IR and Raman activity of vibrational modes. This implies the limitation to non-centrosymmetric media. Therefore, IR-VIS sum frequency spectroscopy provides exclusive spectra of the surface. Since the unpertubated  $[\text{Fe}(\text{CN})_6]^{4-}$  belongs to the point group  $O_h$ , no vibrational mode is SFG active, unless a deformation takes place. A stretch of the ion reduces the symmetry to point groups, which have SFG active modes. The resulting spectra provide evidence for the symmetry breaking induced by surface effects.

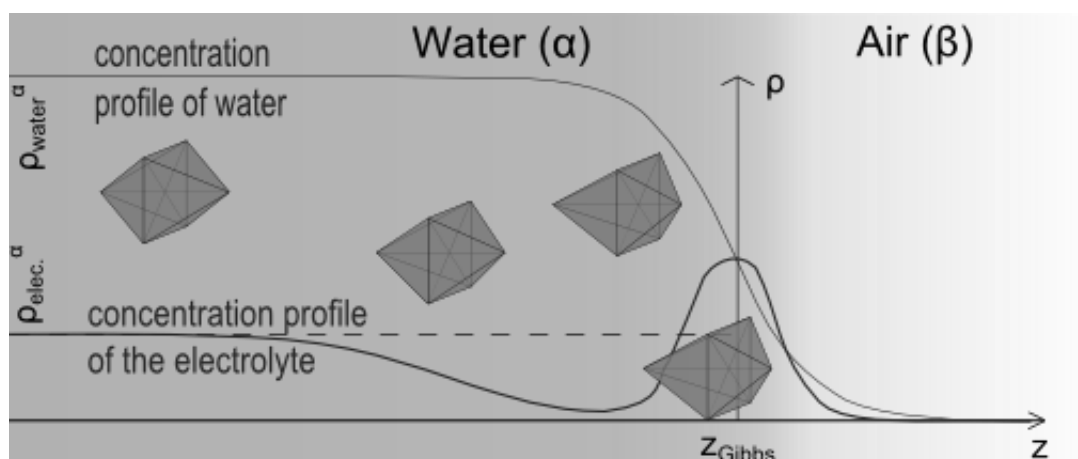


Fig. 1: Schematic representation of the distortion of the octahedral symmetry of hexacyano ferrate at the air water interface due to surface effects. A nonmonotonous concentration profile of the anion is expected.

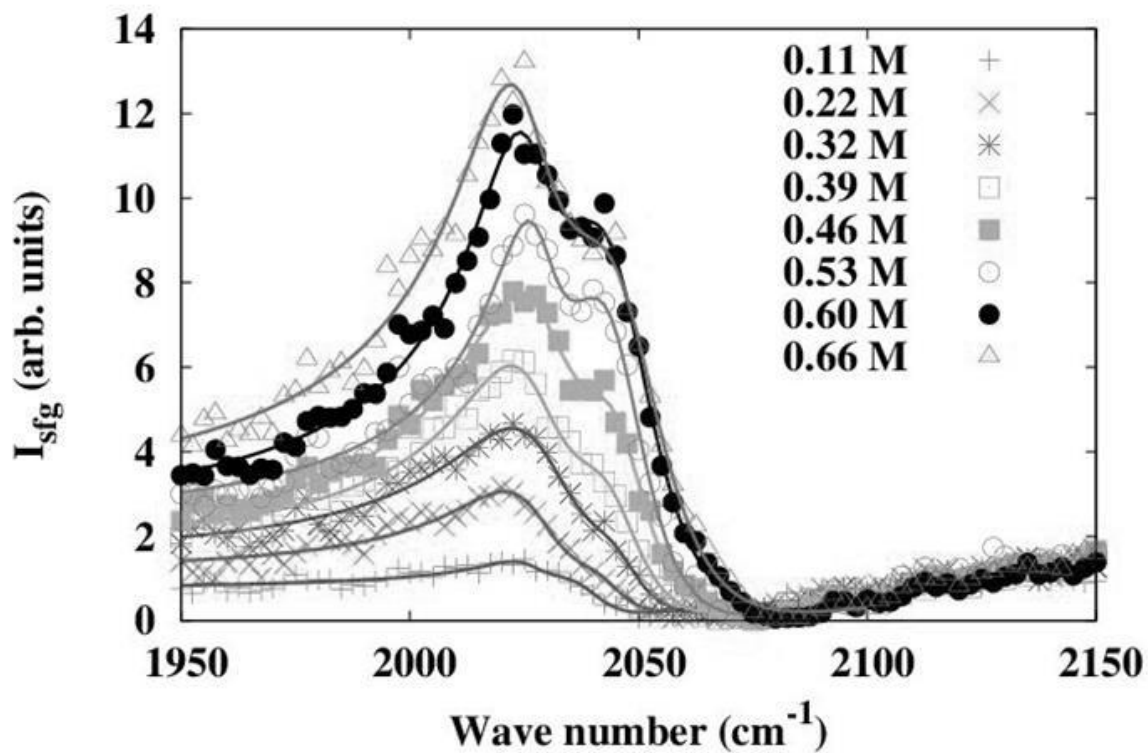


Fig. 2: The spectra shows the SFG active modes of the CN-stretch of  $[\text{Fe}(\text{CN})_6]^{4-}$ . This implies that the ion has no longer the octahedral symmetry.

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***Invited Lecture:***

**Lanthanide-lipid Interactions: Monolayer and other Studies Reveal Two Levels of Ionic Specificity**

Epameinondas Leontidis<sup>1</sup>, Maria Christoforou<sup>1</sup>, Chara Georgiou<sup>1</sup>,  
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We examine lanthanide-lipid interactions using Langmuir monolayers of DPPC and a new double-chain malonamide. Contrary to the popular belief that these interactions are strong, we find them weaker than expected and strongly dependent on the anion of the lanthanide salt. Pressure-area isotherms, Brewster-angle microscopy, grazing incidence X-ray diffraction and IRRAS have been used to study the monolayers. Bulk water studies (ITC, SAXS and fluorescence) involving dodecyl phosphocholine micelles corroborate that the anion of the lanthanide salt has a strong effect on lanthanide-lipid interactions, something which has not been recognized in the literature. Thus, nitrate and sulfate salts have a much stronger interaction with the lipids than chloride salts, and the presence of additional "neutral" electrolytes provides additional strong modifications of the interactions. Such many-tiered effects appear to be general enough for highly charged cations and may be used to change the affinities between ions and interfaces in controlled ways.

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**Oral Presentations**  
**Wednesday, September 10, 2014**

PL03: PLENARY LECTURE

## **Bacteria as Active Colloids - the Physics of Growing and Swimming Rods**

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In terms of length scale, bacteria belong to the colloidal domain. On the other hand, they are alive, and do things that (until recently) synthetic colloids do not do at all - they consume free energy from their environments to engage in growth and division, as well as self-propelled motion (swimming). (Self-propelled synthetic colloids are now available.) Bacteria are therefore *active colloids* - suspensions of particles in which the individual particles are intrinsically out of thermal equilibrium. In this lecture, I will review a number of recent experiments studying bacteria as active colloids, and show that growth as well as motility lead to new kinds of behaviour. In the first half of the lecture, I will introduce a growing colony of *Escherichia coli* as an unstable active liquid crystal of rods, and show that concepts from liquid crystal physics can be used to make sense of some aspects of experimental observations. In the second half of the lecture, I will review the behaviour of swimming bacteria, focussing on how flagellated *E. coli* swim in complex fluids (polymer solutions and gels), and the behaviour of swimming cells confined inside water-in-oil emulsion droplets. Time-permitting, I will also compare the behaviour of swimming *E. coli* and synthetic swimmers (Janus colloids) in an 'obstacle course' in the form of a crystalline array of large, immobile colloidal particles.

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**Supramolecular Assembly and Chain Conformations of Peptide-polymer Conjugates in Solution Studied by Small-angle X-ray Scattering**

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Hybrid biomaterials based on synthetic (polymer) and biological (proteins, peptides) building blocks, called protein-polymer conjugates, provide a range of opportunities for man-made materials to interface with biological system at the molecular level [1]. Encoded by their amino acid sequence, peptides form secondary structures (alpha-helices, beta-sheets) which self-assemble into tertiary structures such as coiled-coil bundles or beta-barrels in a hierarchical manner. For therapeutics, polymer functionalization, often by poly(ethylene glycol), PEG ("PEGylation"), is an effective method to improve the solubility, increase the life time and protect the proteins from the immune system [2]. It is therefore essential to investigate the integrity of the structures, and in particular address the conformation of the polymer chains *in situ*. In this work we consider two families of peptides that are able to form alpha-helical (coiled-coil) bundles [3,4] and beta-sheet fibrils respectively [5]. We show how small-angle X-ray scattering (SAXS) can be efficiently used to characterize detailed structural features including the polymer chain conformation. We will provide an overview of the methodology, specifically addressing model peptides that self-assemble into tertiary structures and relate their solution structure to their crystallographic structure. Particular attention will be given to the effect of PEG and the modification of polymer conformation when attached to the peptides. We will also discuss lipid-modified peptides that form micellar structures.

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## Structure of Nanoparticle-Lipid Multilayers

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Hybrid nanoparticle-lipids multilayers have attracted great interest as potential novel materials for applications such as drug delivery, energy harvesting or sensing, and as model system in fundamental research. Different nanoparticles such as silica, cadmium telluride, or iron-platinum can be incorporated into lipid multilayers in different ways, *e.g.* drop casting from mixed particle-lipid dispersions<sup>1</sup>, adding particles to pre-existing multilayers *via* chemical vapour deposition<sup>2</sup>, and thermal deposition followed by rehydration<sup>3</sup>. To fully explore the potential of lipid-nanoparticle composites, it is important to understand how the structure and stability of lipid multilayers could be affected by the presence of nanoparticles.

In the current work, the structure of 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) and 1,2-distearoyl-*sn*-glycero-3-phosphocholine (DSPC) multilayers were investigated at the mica surface using X-ray reflectometry (XRR). The samples were made by drop casting aqueous mixtures of nanoparticles and lipid liposomes on freshly cleaved mica and then drying them in *vacuo*. Negatively charged polystyrene (24 nm in diameter) and anionic, cationic and neutral 4th-generation poly(amidoamine) dendrimers (~4.5 nm in diameter) were used.

The analysis of the distinct Bragg peaks in XRR curves indicates ordered and polycrystalline domains with tens of bilayers stacked approximately parallel to the substrate. The thickness of single lipid bilayers is ~4-5 nm when dry. The effect of temperature, water addition and the presence of different nanoparticles on the structure of the lipid multilayers will be discussed.

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## **Self-Assembled Short Peptides Nanostructures Utilized in Various Technological Applications**

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Organic and inorganic self-assembled tubular nanostructures were suggested to have key potential in nanotechnological devices and applications. Several studies have shown the possible use of bionanometric material for applications ranging from molecular electronic to drug delivery. The diphenylalanine peptide, the core recognition motif of the Alzheimer's Beta-amyloid polypeptide, efficiently self-assembles into discrete, well-ordered peptide nanotubes.

In the current research, using different microscopy and spectroscopy tools, we describe a remarkable thermal and chemical stability of the aromatic-dipeptide-nanostructures [ADNS]. Furthermore, we studied the peptide nanotubes and nano-spheres mechanical properties and found that the peptide nanospheres have high Young's modulus of up to 275 GPa, which places these peptide nano-assemblies among the stiffest bio-inspired materials presently known.

A limiting factor in the utilization of the ADNS system was the ability to spatially control the assembly process. Various methodologies were developed for the horizontal and vertical alignment of the ADNS and for their patterning. We used the inkjet technology for the application of ADNS on non-biological surfaces. Additionally, vapor-deposition technique was used to form vertically aligned nanotubes arrays that were later utilized for the formation of super-hydrophobic surface, sensitive sensors and ultracapacitors for energy storage applications.

In summary, the remarkable physical properties and the ability to control the assembly of the ADNS suggests their application in conventional microelectronic and microelectromechanics processes, as well as fabrication into functional nanotechnological devices.

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## **New Peptidomimetics at the Interface: Characterising a Powerful Class of Antimicrobial Molecules**

Janos Keller<sup>1</sup>, Simone Mosca<sup>2</sup>, Laura Hartmann<sup>2</sup>, Gerald Brezesinski<sup>1</sup>

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Polymeric biomimetics are important in different biomedical fields including drug delivery and gene transfection as well as many scopes of immunology. While classical polymer synthesis only creates polydisperse polymers with weakly controllable structure and function, the multifunctional peptido- and glycomimetics are monodisperse and perfectly adjustable. That is possible since an increasing toolbox of building blocks is established for the fully automated solid phase peptide synthesizer.

The talk will deal with a novel class of amphiphilic cationic oligoamidoamides also termed  $\beta^{3R3}$ -peptides as very potent antimicrobial agents and will mainly concentrate on the characterization of their physicochemical parameters.

The techniques used involve amongst others Infrared Reflection-Absorption Spectroscopy (IRRAS) and surface pressure measurements to investigate structural features of amphiphilic cationic  $\beta^{3R3}$ -peptide sequences at the soft hydrophobic/hydrophilic air/liquid interface. The position of the amide I band in the IRRA spectra was carefully analyzed. Most of the oligomers showed the band at around  $1660\text{ cm}^{-1}$  characteristic for conformations indicating intramolecular hydrogen bond networks, such as helices. Besides the structural characterization of the pure peptidomimetics, their interaction with different lipid model membranes was also investigated and correlated with the results obtained in biological experiments. The peptides have been injected underneath a pre-compressed lipid monolayer to study the ability of the peptides to penetrate into such layers. All experiments show clearly that this novel class of peptidomimetics combines high and selective antimicrobial activity with exceptionally low cytotoxicity in comparison to values reported in the literature.<sup>[1]</sup>

[1] S. Mosca, J. Keller, N. Azzouz, S. Wagner, A. Titz, P. H. Seeberger, G. Brezesinski, L. Hartmann: Amphiphilic cationic  $\beta^{3R3}$ -peptides: membrane active peptidomimetics and their potential as antimicrobial agents, *Biomacromolecules*, **2014**, DOI: 10.1021/bm500101w

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**On the Role of Hydrophobic Interactions in Cellulose Dissolution and Regeneration: Colloidal Aggregates and Molecular Solutions**

Bruno Medronho<sup>1</sup>, Luís Alves<sup>2</sup>, Björn Lindman<sup>3,4</sup>

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The development of state of the art dissolution/regeneration strategies for cellulose constitutes an increasingly active research field. These are fundamental aspects of many production processes and applications. A wide variety of suitable solvents for cellulose are already available, however, these are of highly different nature giving great challenges in the understanding of the subtle balance between the different interactions. Insolubility is often attributed to strong intermolecular hydrogen bonding between cellulose molecules. However, our recent work rather emphasizes the role of hydrophobic interactions. Here, we report the effect of two different solvents on the dissolution of cellulose on multiple length scales and its consequences on the characteristics of the regenerated material. While an aqueous tetraalkylammonium hydroxide solution gives rise to what appears to be dissolution down to the molecular level, the cold alkali solvent (NaOH based) does not dissolve cellulose molecularly but rather leaves aggregates of high crystallinity stable in the cellulose dope. It is suggested that such striking difference in the solubility pattern resides in the hydrophobicity of the tetraalkylammonium cation (contrasting to the polar inorganic cation of the alkali system) which is capable of weaken the hydrophobic interactions in cellulose solubilizing the biopolymer molecularly.

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## The Amphiphilic Character of Cellulose Molecules Dissolved in Solvent Mixtures Containing Ionic Liquid and Its Utilization in Emulsification

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Cellulose is the most abundant renewable material in nature that is utilized as a raw material for fabrication of synthetic products. Although it is not soluble in common solvents, there is significant interest in the use of solvent mixtures containing ionic liquids (IL) and polar organic solvents for cellulose dissolution. We present evidence for true molecular dissolution of cellulose in binary mixtures of common polar organic solvents with an ionic liquid, using cryogenic transmission electron microscopy, small-angle neutron-, x-ray- and static light scattering. In particular, the measured low values of the molecular weight ( $M_w$ ), gyration radius ( $R_g$ ) and persistence length indicate the absence of significant aggregation of the dissolved chains.

We conjecture that the dissolved cellulose chains are amphiphilic. This can be inferred from the facile fabrication of cellulose-encapsulated colloidal oil -in-water or water-in-oil dispersions. This may be done by mixing water, oil and cellulose solution in an ionic liquid. A more practical alternative is to form first a hydrogel from the cellulose/ionic liquid solution by coagulation with water and applying it to sonicated water /oil or oil /water mixtures. Apparently the dissolution/regeneration process affords higher mobility to the cellulose molecules so an encapsulating coating can be formed at the water-oil interface.

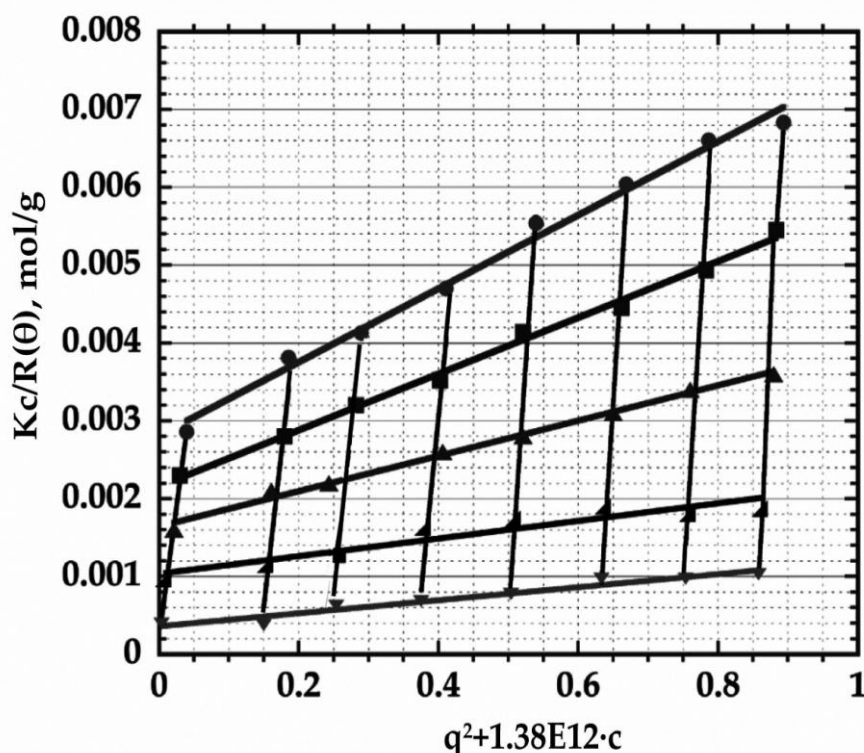


Fig. 1. Zimm plot of cellulose solutions in N-dimethyl formamide/1-ethyl-3-methylimidazolium acetate (9:1 molar ratio), yielding molecular weight  $M_w \sim 50$  kDa,  $R_g \sim 36$ nm and second virial coefficient  $A_2 \sim 0.025$  mol $\cdot$ ml/g $^2$

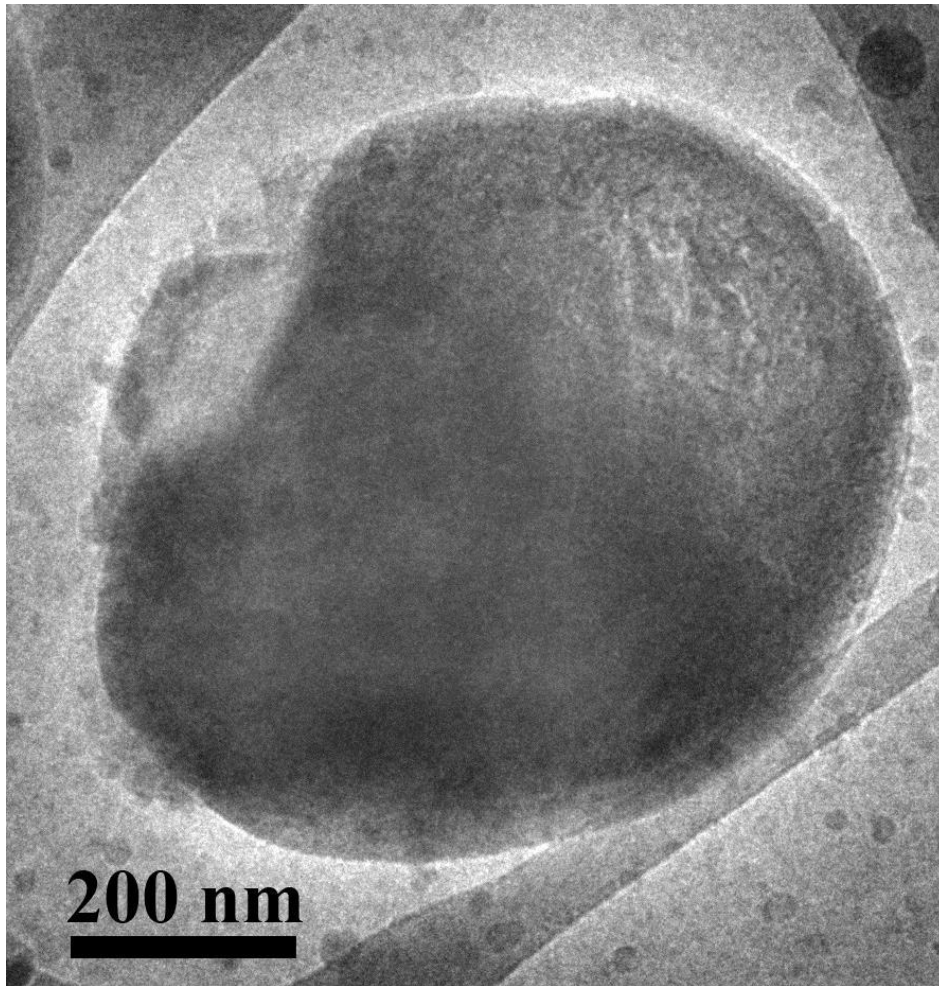


Fig. 2. shows a cryo-TEM image of a vitrified thin film of an aqueous dispersion of cellulose-coated paraffin oil.

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**Keynote Lecture:**  
**DNA-based Gels and Nanoparticles**

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A general understanding of the interactions between DNA and oppositely charged agents, and in particular of their phase behaviour, has provided a basis for developing novel DNA-based materials, including gels and gel particles. DNA associates strongly with cationic cosolutes, such as surfactants, lipids, polymers and proteins; all these systems are characterized by a strong associative phase separation.

The binding patterns for several systems are presented, illustrating the consequences of this binding in solution, in terms of phase behaviour, compaction/decompaction and microstructure.

Plasmid DNA gels have been prepared and investigated with respect to their swelling/deswelling in aqueous solution containing different additives, such as metal ions, surfactants, polyamines, proteins and drugs. It was found that covalent gels offer novel opportunities for monitoring DNA-cosolute interactions. The photodisruption of pDNA gels was used as a strategy to promote controlled pDNA release. Cell viability assays also suggest that the pDNA gels are biocompatible.

Based on the associative phase separation and interfacial diffusion, we have also developed a way to prepare DNA gel particles without adding any kind of cross-linker or organic solvent; and the preparation of DNA particles, by just mixing DNA with surfactant, polycation and protein solutions, has been achieved. Surface morphology, degree of DNA entrapment, swelling/deswelling behaviour and kinetics of DNA/protein release are also described. The stronger interaction of ssDNA, as compared with dsDNA, suggests the important role of the amphiphilicity of DNA on the interactions. These DNA gel particles were also assessed for haemolysis.

It is our belief that these findings may increase the potential of these systems as delivery and co-delivery systems.

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## **Mechanically Robust Slippery Liquid-Infused Porous Surfaces Based on Electrodeposited Porous Tungsten Bronze Films**

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A simple, nontoxic and inexpensive method to prepare mechanically robust surfaces that repels a variety of liquids and solids has immediate relevance in many industrial applications. Unwanted interactions between liquids and surfaces are currently a limiting factor nearly everywhere liquids are handled or encountered. Most state-of-the-art liquid repellent surfaces are modeled after lotus leaves, which are known to exhibit superhydrophobicity and self-cleaning. Despite over a decade of research, these surfaces are still plagued with problems that restrict their practical applications.

Recently, the slippery liquid-infused porous surfaces (SLIPS) technology was introduced by our group. SLIPS technology is inspired by the *Nepenthes* pitcher plant and provides unique capabilities that are unmatched by any other liquid-repellent surface technologies. SLIPS surfaces function under high pressure conditions, instantly self-heal imperfections, provide optical transparency, repel ice nucleation, and are ultra-repellent to pure and complex fluids such as blood, crude oil, and brine. They also repel solids such as ice and wax. These properties allow the slippery surfaces to be used in a wide variety of applications and environments. Moreover, the slippery surfaces can be constructed from a broad range of simple, inexpensive materials without the need for specialized fabrication facilities.

Here we used a stainless steel, which is widely used in biomedical, household and industrial equipment, surgical instruments, kitchen appliances, transport and architecture, as a substrate. Inexpensive and environmentally friendly electrodeposition process used to form a thin layer of nanostructured tungsten bronze. Such films are mechanically robust and can be functionalized to increase its hydrophobicity, ideal for integration with SLIPS technology. Moreover, electrochemical deposition provides various control parameters for optimization of the film morphology. We will present that slippery stainless steel surfaces can be optimized to repel simple and complex fluids, reduces ice formation, accelerates frost removal and prevent adhesion of biofilms.

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## **Kinetics of CO<sub>2</sub> Exchange through Water-Air Interfaces within a Closed Finite-Size System**

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We study a few physical phenomena that are relevant mostly to carbonated beverages, and partly to problems of CO<sub>2</sub> sequestration [1]. Our experiments and analysis include the chemically most simple case of a water-CO<sub>2</sub> solution (a "pure soda"), but equally apply to real sparkling beverages such as Champagne, beers and colas. Our goal is to understand the kinetics of CO<sub>2</sub> exchange through the liquid-gas phase interface, in response to e.g. a transient change in pressure or to mechanical perturbation. We thus address frequently asked and apparently simple questions about how fast the liquid inside can ingest or reject carbon dioxide, how opening of a Champagne bottle modifies the gas content inside, and what is the consequence of shaking the bottle on the pressure and the later occurrence of effervescence and gushing. We report observations from a set of dedicated experiments, whereby CO<sub>2</sub> pressure, concentration, and convection flows are visualized. The experiments reveal the onset and destabilization of diffusion fronts, and the effect of bubbling induced by shaking on internal pressure. Results are rationalized through considerations involving molecular diffusion, Rayleigh-Taylor instability [1] and the Epstein-Plesset [2] mechanism of soluble gas bubble kinetics.

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[2] P.S. Epstein and M.S. Plesset, *J. Chem. Phys.* **18**, 1505 (1950)

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## **Acoustic Spreading of Water Films – Balancing Capillary and Convective Forces**

Ofer Manor, Gennady Altshuler

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Substrate vibrations at frequencies comparable to HF and VHF radio frequencies and in contact with a liquid generate flow at micron and submicron scales that may lead to spreading of liquid films – acoustic spreading. This spreading mechanism is thought as a way of manipulating liquids and especially water, a natural carrier of biological and biochemical agents, on microfluidic platforms. Acoustic spreading was recently observed under the influence of piston-like substrate motion [1] and surface acoustic waves [2], where vibrational convective forces, invoked near the liquid/solid/air contact line, are found to drive steady contact line motion.

Previous studies on acoustic spreading concentrated on low surface tension liquids, i.e., silicon oil, where spreading is continuous as long as liquid and substrate vibrations are in contact. Water films under acoustic excitation, however, were observed to spread to a minute extent and only under high power levels that further invoke capillary instabilities [3]; physical mechanisms associated with acoustic spreading of water and other high/intermediate surface tension liquids are not well understood and are the topic of this presentation.

We will discuss acoustic spreading of liquid films with arbitrary surface tension. We will bridge between the mechanisms associated with acoustic spreading of low and high surface tension liquids and show that film spreading is governed by a balance between capillary and convective forces. This analysis elucidates the discrepancy, observed in earlier studies, between the response of oil and deionized water to acoustic excitation and further highlights an intermediate region, where precise manipulation of the rate and direction of liquid spreading is achieved by carefully balancing governing mechanisms.

[1] O. Manor, et al; *Soft Matter* 2011, 7, 7976

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[3] D. Collins, et al; *Phys. Rev. E* 2012, 86, 056312

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**Self-Assembly in an Evaporating Nanofluid Droplet: Rapid Transformation of Nanorods into 3d Fibre Network Structures**

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<sup>1</sup>*School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai, China*

<sup>2</sup>*School of Chemistry, University of Bristol, Bristol, UK*

Evaporative drying of a particle-laden droplet is an everyday phenomenon and is also widespread in industrial and technological processes. It can produce a plethora of residual surface patterns, including multiple rings, regular stripes, multilayer deposit and, most commonly, coffee rings. Recognised as a simple and versatile method for the organization of materials of interest (polymers, nanoparticles and biomaterials) into sophisticated structures, the subject of controlled evaporative self-assembly (CESA) continues to be topical and academically and technologically important.

Here we report unexpected and unprecedented residual surface patterns from a CESA process – very different from those previously reported. When a tiny droplet of a nanofluid containing ZnO nanorods dries on a glass slide at room temperature, we find that, within tens of seconds, a uniform thin film with a 3D porous network structure comprising centimetre-long Zn(OH)<sub>2</sub> nanofibres can spontaneously form. The observation of this rapid chemical (ZnO → Zn(OH)<sub>2</sub>) and morphological (nanorods → cm-long fibres) transformation of a drying nanofluid is surprising and striking in itself, but more importantly, reveals a new mechanism which is very different from that associated with the coffee rings, as we elucidate in this presentation. Our results point to a facile route for generating self-assembled 3D structures with ultralong nanofibres, important to a range of modern technologies.

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**Imaging of Capillary Bridges and Measuring Capillary Forces Simultaneously**

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 Michael Kappl, Doris Vollmer, Hans-Jürgen Butt  
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 Germany*

Capillary bridges play a important role for the stability of colloidal systems. The forces of these bridges strongly correlates with their shape. It is possible to measure capillary forces with an Atomic Force Microscope (AFM), but it is impossible with such a device to image the shape of the capillary bridge at the same time. Analytical and numerical calculations exist that correlates the force of the capillary bridges with the shape of the liquid. However experimentally capillary bridges couldn't directly be imaged with the corresponding force in the micrometer range so far. A Laser Scanning Confocal Microscope (LSCM) can visualize the shape of a liquid bridge on solid surface in a three-dimensional form. Our aim is to bring both techniques, AFM and LSCM, together. Because the changes in shape of the menisci due to the force measurements with the AFM are in the range of  $\mu\text{m/s}$ , the LSCM must ensure a high image acquisition rate, which is possible to realize with a resonant scanner. We built a combined LSCM and AFM device and measured the forces with colloidal probes on liquid surfaces. In comparison to commercially available devices we are also able to image fast dynamics (up to 20 images per second). The combination of force spectroscopy and confocal microscopy allows us to image capillary bridges and simultaneously measure the corresponding force (Figure1) . We present the first results of simultaneous measurements of capillary bridges and the corresponding force curves.

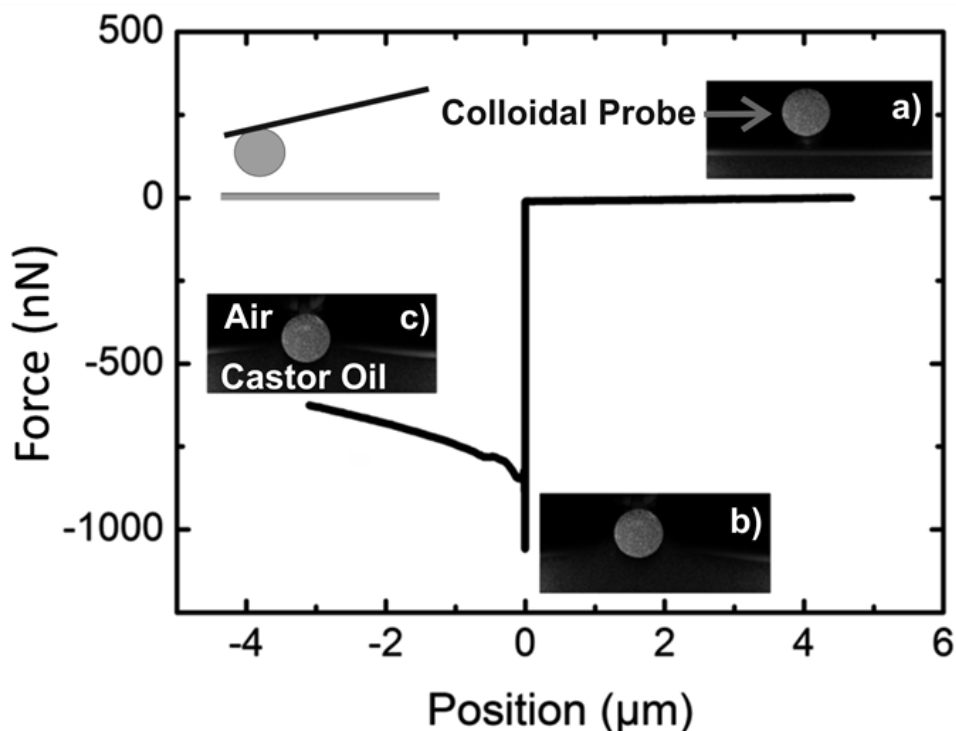


Figure 1: Force Curve of a Colloidal Probe Measurement with Corresponding Confocal Images as Inset. a) Colloidal Probe approaches to the surface, b) Colloidal Probe touches the Liquid c) Colloidal Probe retracts from the liquid. Image Size of Confocal Images:  $156\mu\text{m} \cdot 68\mu\text{m}$ , Silica-Particle Diameter:  $32\mu\text{m}$ , Liquid: *Castor Oil*.

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***Invited Lecture:***

**Capillary Bridge Dynamometry - Method for Quantifying the Anisotropic Surface Stresses in Elastic Interfacial Layers and their Adhesion to Solid Surfaces**

Peter Kralchevsky<sup>1</sup>, Krassimir Danov<sup>1</sup>, Rumyana Stanimirova<sup>1</sup>,  
Elka Basheva<sup>1</sup>, Krastanka Marinova<sup>1</sup>, Theodorus Blijdenstein<sup>2</sup>,  
Simeon Stoyanov<sup>2,3</sup>

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Dense protein adsorption layers at air/water and oil/water interfaces, and phospholipid membranes possess surface shear elasticity. Because of that, the stresses in such interfacial layers are, in general, non-uniform and non-isotropic. With them, the method of axisymmetric drop/bubble shape analysis, based on the Laplace equation with isotropic surface tension, fails. To determine the meridional and azimuthal stresses in each point of the surface of a pendant drop/bubble covered with an elastic layer, we developed a new method, capillary meniscus dynamometry. It is based on measurements of (i) the shape of a bubble/drop formed on the tip of a capillary and (ii) of the capillary pressure of this bubble/drop [1], followed by nontrivial data processing based on the interfacial-stress-balance equations, without making any rheological-model assumptions. After pressing the bubble/drop against a solid plate (substrate), it forms a capillary bridge between the substrate and the capillary tube (Fig. 1). The bridge profile is subjected to the same procedure of data processing, which gives not only the acting local interfacial stresses at each moment of time, but also the force of bubble/drop adhesion to the substrate (capillary bridge dynamometry). The method is tested with bubbles and drops covered by surfactant and protein adsorption layers. It could be applied to quantify the effect of different factors and additives on the surface elasticity and adhesion to substrates.

[1] S.C. Russev, N. Alexandrov, K.G. Marinova, K.D. Danov, et al. *Rev. Scientific Instruments* **79** (2008) 104102.



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**Oral Presentations**  
**Thursday, September 11, 2014**

## Hybrid Nanomaterials for Biomedical Applications

Luisa De Cola

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The talk will focus on the synthesis, characterization and applications of porous organosilicates, silicates, to be used for in vitro and *in vivo* imaging but also as components for special type of hydrogels. The use of ordered mesoporous silica will be illustrated as containers for molecules and for delivering PNA and DNA inside HeLa cells. The fate of the silica particles will be discussed and in particular their accumulation in specific location in the cells will introduce our newest finding of porous systems able to disintegrate upon an external stimulus. Their delivery properties and their destruction kinetics shown with an example. I will discuss the use of small porous nanoparticles, as constituent of hydrogel, to generate hybrid scaffold used as matrix for 3D growth of cells. The pores of the particles can be used as food reservoir and we have demonstrated that cells in such conditions can live several days.

1. A. Bertucci, H. Lülfi, D. Septiadi, A. Manicardi, R. Corradini, L. De Cola, *Adv. Healthcare Mater.*, **2014**
2. F. Fiorini, L. De Cola to be submitted

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## **Photocontrol of Colloidal Deposition from Evaporating Drops with Optically-Tunable Particle Stickiness**

Manos Anyfantakis<sup>1,2,3</sup>, Damien Baigl<sup>1,2,3</sup>

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When a coffee drop dries on a solid, a ring pattern is usually observed as most of the suspended particles gather at the drop periphery [1]. The so-called coffee-ring effect (CRE) is a ubiquitous phenomenon observed in any pinned evaporating drop containing non-volatile solutes. Despite the vivid interest in controlling the CRE, methods reported so far were based on adapting the drop composition [2] and solute characteristics [3], hindering any reconfigurability for a given system. Additionally, on-demand modulation of the deposit profile has not been yet demonstrated.

An alternative strategy is the use of external stimuli which can affect the drying process. Photocontrol of particle deposition emerges as an advantageous candidate, since light offers a contact-less and highly reconfigurable stimulus. Here, a novel optical approach to dynamically control particle deposition from evaporating drops is presented. We designed aqueous suspensions consisting of nanoparticles and photosensitive surfactants where the attractive particle interactions ('stickiness') can be modulated by LED light. An increase in particle stickiness favours particle-particle attraction and trapping at the liquid/gas interface, which results in deposit homogenization. A wide range of patterns from rings to homogeneous disks is achieved by varying the irradiation time that directly controls particle stickiness. Patterning from single drops is photoreversible upon changing the wavelength while spatial control in multi-drop arrays is achieved using a photomask. The reported effect is robust as evidenced from the excellent pattern reproducibility [4].

### References:

- [1] R. D. Deegan et al., *Nature*, 389, 827-829 (1997)
- [2] H. Hu and R. G. J. Larson, *Phys. Chem. B*, 110, 7090-7094 (2006)
- [3] P. J. Yunker et al., *Nature*, 476, 308-311 (2011)
- [4] M. Anyfantakis and D. Baigl, *submitted*.

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## Investigation of the Structural Dependence of Mesoporous Silica Functionalized with Carboxylic Groups

Ruiyu Lin<sup>1</sup>, Shunai Che<sup>2</sup>, Karen Edler<sup>3</sup>, Michael W. Anderson<sup>4</sup>,  
Viveka Alfredsson<sup>1</sup>

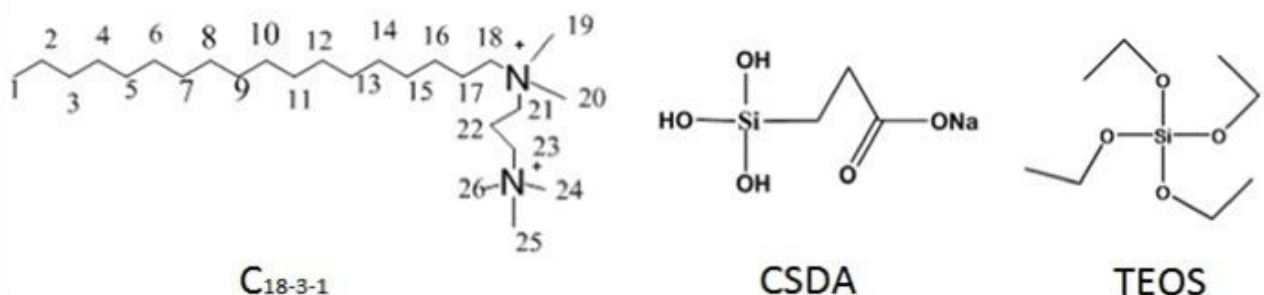
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We aim at obtaining a molecular understanding for the mechanism responsible for the formation of mesoporous silica functionalized with carboxylic groups<sup>1</sup>. The materials are synthesized under aqueous conditions using a cationic surfactant (C<sub>18-3-1</sub>) as structure director, a co-structure directing agent (CSDA) and with tetraethylorthosilicate (TEOS) as silica source. The structures of the materials are dependent on the amount of HCl added in the synthesis. With increasing amount of HCl the structure transforms from (pH about 9) *Fm-3m* structure, to *Fd-3m* structure (pH about 6)<sup>2</sup>. The silica network forms in a polymerisation reaction involving siliceous species, obtained after TEOS hydrolysis (producing siliceous species and ethanol), and the siliceous part of CSDA. The formation of the mesoporous structures rely on the self-assembly of the surfactant micelles and the silica network/species.



We have investigated the structural effect of TEOS hydrolysis. In two separate investigations we have either promoted the hydrolysis step, by introducing a pre-hydrolysis step, or slowed down the kinetics by addition of ethanol to the synthesis solution.

We conclude that the formation process is more complicated than has been postulated<sup>1</sup>. Pre-hydrolysis of TEOS results in the *Fm-3m* structure regardless of pH. When the hydrolysis is slowed down, by the addition of ethanol, the *Fd-3m* structure is more easily obtained. Hence, the hydrolysis rate is the important structural control parameter.

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[2] Y. Sakamoto, et al. *Chem. Mater.*, **2009**, *21*, 223-229.



## **Hierarchically Organized Layers of Phospholipids and Proteins in Electrolyte-Gated Transistors: Where Soft Matter and Organic Electronics Meet**

Gerardo Palazzo<sup>1</sup>, Donato De Tullio<sup>1</sup>, Maria Magliulo<sup>1</sup>, Mulla Yusuf Mulla<sup>1</sup>,  
Francesca Intranuovo<sup>1</sup>, Pietro Favia<sup>1</sup>, Inger Vikholm-Lundin<sup>2</sup>, Luisa Torsi<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Bari, Bari, Italy*

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Soft matter systems interfaced to an electronic device are presently one of the most challenging research activity that has relevance not only for fundamental studies but also for the development of highly performing bio-sensors. In this presentation the full integration of hierarchically organized layers phospholipid bilayers and proteins into an electrolyte gated organic field effect transistor (EGOFET) is proposed.

In EGOFETs, the dielectric gating is achieved through the formation of a Debye-Helmholtz double layer (DHDL) at the interface between the electrolyte solution and the OSC layer. Being very thin (few Å) such DHDL has a large capacitance allowing for sub-volt operation. We have functionalized the OSC by anchoring on it a biotinylated phospholipid bilayer [1]. The supported bilayer can be easily further functionalized with virtually any receptors by using biotin-streptavidin chemistry. Actually, we have functionalized the EGOFET with an antibody against the C-reactive protein (CRP) thus obtaining a transistor device able to sense the CRP concentration. The device performances improve upon increasing the high ionic strength of the electrolyte solution thus allowing the sensing also on blood serum. This result challenges the current believe that electronic detection is unsuited to sense any recognition event taking place at a distance from the semiconductor surface much larger than the Debye's length. The sensing mechanism that allows to circumvent the screening due to the background electrolytes will be discussed

[1] M. Magliulo, A. Mallardi, M. Yusuf Mulla, S. Cotrone, B.R. Pistillo, P. Favia, I. Vikholm-Lundin, G. Palazzo, L. Torsi

**Electrolyte-Gated Organic Field-Effect Transistor Sensors Based on Supported Biotinylated Phospholipid Bilayer**

*Adv. Mater.* **2013**, 25, 2090–2094

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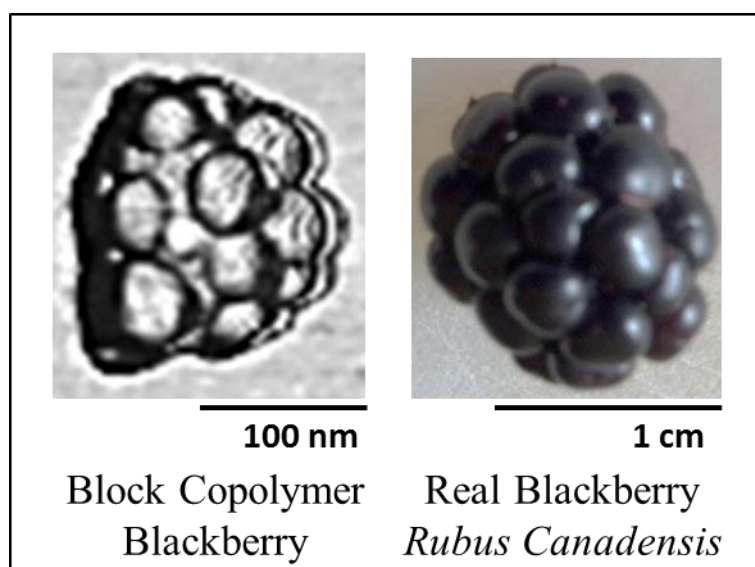
## Blackberry-Shaped Block Copolymer Aggregate Capsules

Adi Eisenberg<sup>1</sup>, Renata Vyhalkova<sup>1</sup>, Lin Xiao<sup>2</sup>, Guang Yang<sup>2</sup>

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<sup>2</sup>*Department of Biomedical Engineering, Huazhong University of Science and Technology, Wuhan, China*

The preparation and properties of nano-sized blackberry-type structures are described. The capsules are composed of two types of block copolymer aggregates, a relatively large core vesicle, onto which is deposited a layer of smaller vesicles or micelles. The composition of the adjacent layers is such as to assure strong electrostatic interactions between them. The core vesicles can be composed of either PS-*b*-P4VP with a positively charged corona or of PS-*b*-PAA with a negatively charged corona, and can be surrounded by a layer of smaller, oppositely charged block copolymer vesicles or micelles. These composite structures bear a strong resemblance to blackberries, hence the proposed name. The blackberry structures can be prepared in solution or on a flat surface, e.g. a silicon wafer. Four compositional possibilities for the blackberries structures were studied, in which the positively or negatively charged core vesicles are covered either by a layer of oppositely charged micelles or vesicles. These structures represent the earliest stage of a layer-by-layer approach of small spherical aggregates onto a larger spherical hollow core. The strong interaction between the contacting layers is achieved by electrostatic interactions or by complementary acid-base properties, e.g. H-bonding. These multi-compartmented capsules are worth exploring as delivery vehicles for multiple components; each layer of the capsules could be loaded with hydrophobic (in the core of the micelles or vesicle wall) or hydrophilic molecules (in the vesicle cavity). The overall size of such structures can be kept below one  $\mu\text{m}$ .



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***Invited Lecture:***  
**Water-Based Noncovalent Nanomaterials**

Boris Rybtchinski

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Self-assembled nanoscale systems that are robust yet adaptive and prone to facile fabrication and reversible disassembly are of primary importance for creating multifunctional adaptive nanomaterials. We will present our work on water-based recyclable noncovalent membranes that can be used for size-selective separations of nanoparticles and biomolecules,<sup>1,2</sup> advancing a paradigm of noncovalent nanomaterials as a versatile and environmentally friendly alternative to covalent systems.<sup>3</sup> We will also describe emerging rational design principles for creating highly ordered functional nanoarrays assembled from well-defined molecular units in aqueous media,<sup>4,5</sup> enabling a general approach towards complex water-based materials.

Krieg, E.; Shirman, E.; Weissman, H.; Shimoni, E.; Wolf, S. G.; Pinkas, I.; Rybtchinski, B. *J. Am. Chem. Soc.* **2009**, *131*, 14365-14373.

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Shahar C.; Baram J.; Tidhar Y.; Weissman H.; Cohen S.; Pinkas I.; Rybtchinski B. *ACS Nano* **2013**, *7*, 3547-3556.

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***Keynote Lecture:***  
**Assembling Anisotropic Magnetic Nanoparticles, or a Colloidal Analogue of Atomic Spin Systems**

Ilya Martchenko<sup>1</sup>, Jérôme J. Crassous<sup>1</sup>, Erik Wernersson<sup>1</sup>, Hirt Ann<sup>2</sup>,  
Herve Dietsch<sup>3</sup>, Per Linse<sup>1</sup>, Peter Schurtenberger<sup>1</sup>

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We have determined the phase diagram of magnetic colloidal ellipsoids as a function of both packing fraction  $\phi$  and external magnetic field  $B$ . We use core-shell particles with a magnetic core where the magnetic moment of the core is sufficiently small to avoid additional dipole-dipole interactions, but high enough to induce preferential particle alignment with an external magnetic field. By using a combination of small-angle x-ray scattering (SAXS) and magnetometry we have examined positional correlations of the charged ellipsoids (aspect ratio  $p = 2.3$ ) and orientational order of their magnetic moments. By combining SAXS and computer simulations we have established structural criteria for the different phase and arrest transitions and map distinct isotropic, polarised fluid and nematic phases over an extended range of  $\phi - B$  coordinates. We demonstrate that upon the isotropic-nematic transition of the ellipsoids, the bulk magnetic behavior of the suspensions switches from superparamagnetic to ferromagnetic. We extend the often-used atom-colloid analogy to spin systems and present a relationship between the structural topology of suspensions of magnetic colloids and their macroscopic magnetic response.

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### **Why Particles are the Better Surfactants - Pickering Type Foams**

Adrian Carl, Anne Bannuscher, Judith Witte, Regine von Klitzing  
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Germany*

Particle stabilized foams are an interesting type of dispersion with applications in various fields of technology from mineral processing to the food industry. Nevertheless, the detailed mechanisms of how (nano)particles stabilize foams are not fully resolved, yet. It has been shown that combining nanoparticles and suitable surfactants can lead to increased foamability and foam stability compared to the surfactant-only system without nanoparticles.

As a model system, we use hydrophilic silica nanoparticles that do not attach to the water/air interface until they are modified with alkylamines which render them hydrophobic, so they become surface active. The particle hydrophobicity was adjusted by varying the amount of adsorbed amine and/or the carbon chain length.

The systems were characterized at various length scales from the nanometer to the centimeter scale. Results from surface pressure isotherms suggest the formation of a colloidal network around the air bubbles, whereby the network density correlates strongly with the foamability. We determine the contact angle of the nanoparticles at the air water interface via x-ray reflectivity. Diffusing wave spectroscopy was used to probe the particles inside the foam as well as the system's temporal evolution.

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### **Marangoni Flow with Water-Soluble Surfactants**

Sébastien Le Roux<sup>1</sup>, Matthieu Roche<sup>2</sup>, ZhenZhen Li<sup>2</sup>, Ian Griffiths<sup>3</sup>,  
Isabelle Cantat<sup>1</sup>, Arnaud Saint-Jalmes<sup>1</sup>, Howard A. Stone<sup>2</sup>

<sup>1</sup>*Institut de Physique de Rennes, Université Rennes 1, Rennes, Bretagne, France*

<sup>2</sup>*Mechanical and Aerospace Engineering, Princeton University, Princeton, USA*

<sup>3</sup>*Oxford Centre for Collaborative Applied Mathematics, Oxford University, Oxford, UK*

Amphiphiles, such as alcohols, lipids and soaps can decrease the interfacial tension between water and other fluids, thus helping for the compartmentalization of matter in emulsions, foams, vesicles and cells. A difference in the concentration of amphiphiles along an interface between two media triggers an interfacial-tension-induced Marangoni flow whose occurrence is critical for transport phenomena in lipid nanotubes, the stability of emulsions and foams, pulmonary surfactant replacement therapy, insect locomotion and many industrial applications. Although most amphiphiles found in nature and used in the industry have a finite solubility in water, only few studies deal with Marangoni flows induced by water-soluble amphiphiles, while simultaneously considering the effect of the amphiphile finite solubility.

Here we provide a quantitative description of a model Marangoni flow, induced by the spreading and dilution of a local surfactant excess, both in terms of surfactant physicochemistry and hydrodynamics. We show experimentally that i) the spreading Marangoni flow induced by surfactants of finite solubility in water extends over a finite distance and ii) this distance varies monotonically with the critical micellar concentration (CMC). We provide evidence that the velocity field of this flow has universal features, and we identify the scaling laws that capture both the extent over which the Marangoni flow is observed and the magnitude of the maximum velocity.

These results are important for a better understanding of transport phenomena involving amphiphiles at liquid interfaces in out-of-equilibrium systems. In addition, our experimental approach could be adapted to design a new method to measure the critical micellar concentration of an amphiphile.

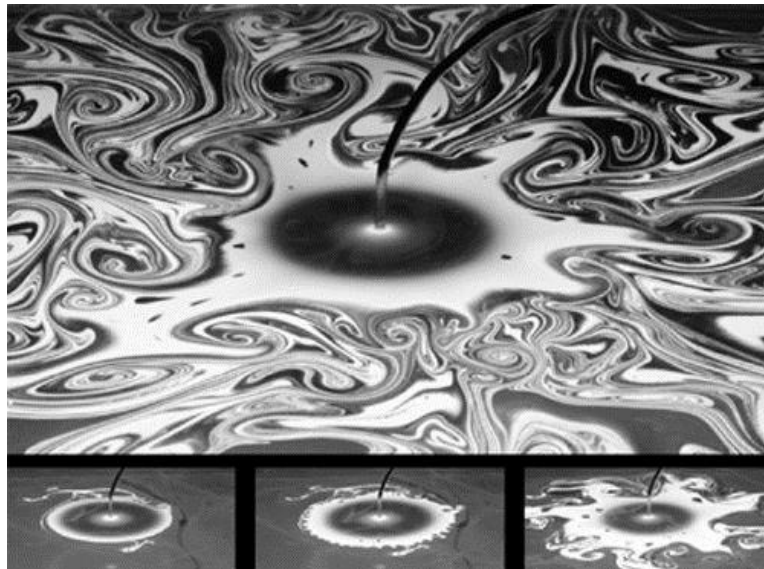


Figure 1: Finite distance of the spreading Marangoni flow for surfactant of finite solubility: a surfactant solution is deposited on top of the liquid at constant rate, and oil droplets act as passive tracers to visualize the flow.

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**Temperature Effect on Foamability, Foam Stability, and Foam Structure of Milk**

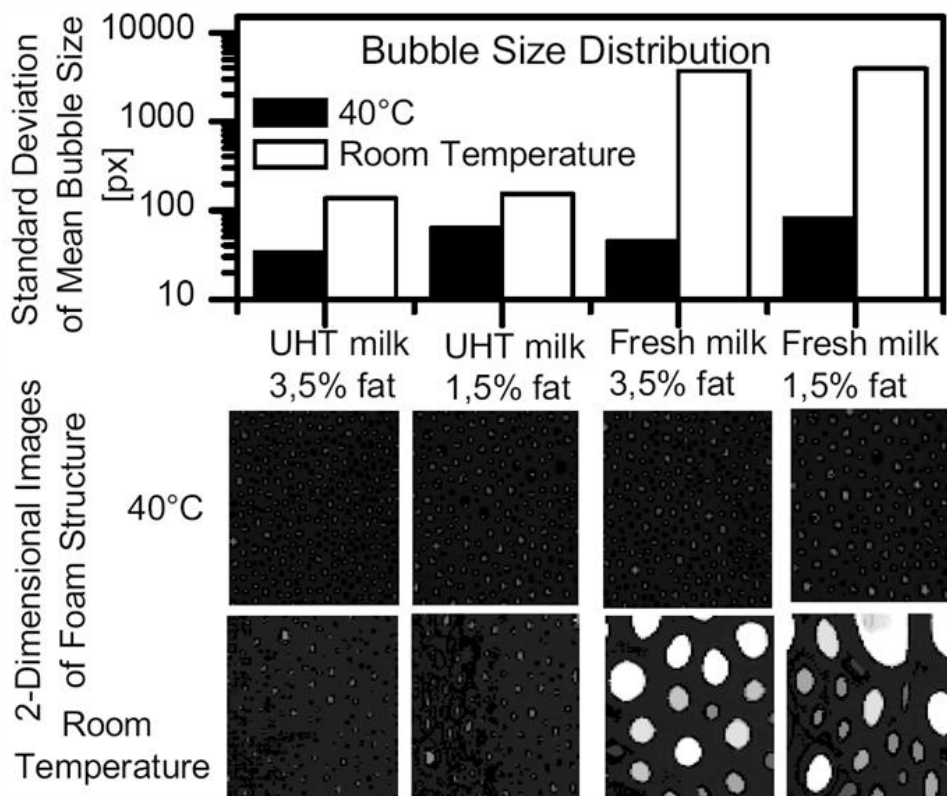
Katrin Oetjen<sup>2</sup>, Christine Bilke-Krause<sup>2</sup>, Mania Madani<sup>1</sup>, Thomas Willers<sup>2</sup>

<sup>1</sup>*Institute of Chemical Engineering and Macromolecular Chemistry,  
University of Hamburg, Hamburg, Germany*

<sup>2</sup>*Surface Science Center, KRÜSS GmbH, Hamburg, Germany*

Milk is a daily consumed product and its intriguing foaming properties are important e.g. when processing dairy-based foams such as whipped cream or cappuccino-style beverages. Dairy foams are colloidal systems formed by air bubbles, water, and surface active proteins. Temperature is a very important parameter influencing the foaming behavior of milks containing lipids[1,2]. We investigated the temperature dependence of foamability, foam stability and foam structure between 5 and 60°C for four types of milk: ultra-high temperature processed milk and pasteurized milk, each with 1.5 and 3.5% fat content. All foam measurements were performed using the KRÜSS DFA100. We found, that foamability and foam stability exhibit a strong minimum at 25°C thereby extending the existing literature with novel data[3]. These and our temperature dependent dynamic surface tension data of the investigated milks support the idea[1], that the state of the milk-fat globule is responsible for detrimental effects on the foaming behaviour. In this talk, we explain how at ~25°C the partially crystalline state of the milk-fat globules negatively affects foaming properties.

Finally, we determined for the first time the temperature and time dependence of the foam structure (bubble size distribution) for all investigated milks[3]. With this the aging behaviour of the foams can be characterized and differences in foam structure's homogeneity can be related to foam stability.





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(accepted, in Press)

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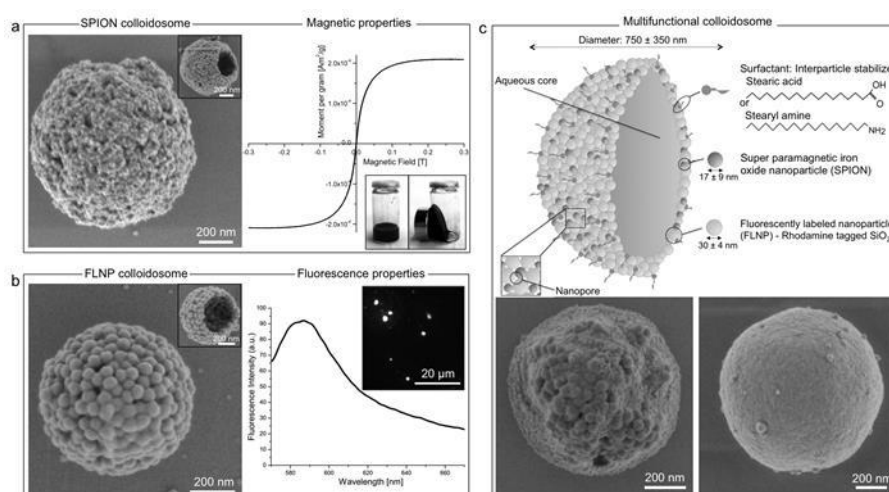
## Multifunctional Submicron Colloidosomes from Fluorescent and Superparamagnetic Nanoparticles for Theranostics

Tobias Bollhorst<sup>1</sup>, Shakiba Shahabi<sup>1</sup>, Charlotte Petters<sup>2</sup>, Ralf Dringen<sup>2</sup>, Michael Maas<sup>1</sup>, Kurosch Rezwan<sup>1</sup>

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Submicron colloidosomes are a promising new type of microcapsule with the potential to significantly improve the field of nanomedicine. Colloidosomes consist of a semipermeable shell of self-assembled colloidal particles. The shell exhibits small pores that are formed between the individual nanoparticles that may allow a controlled release of encapsulated active agents.<sup>1</sup> In our previous work, we demonstrated the synthesis of colloidosomes with diameters below 1  $\mu\text{m}$  based on a single kind of nanoparticle like metal oxides<sup>2</sup> or nanodiamonds.<sup>3</sup> Now, we introduce multifunctional submicron colloidosomes using nanoparticles with distinct physical properties that are formed by the combined assembly from different kinds of nanoparticles.



First, by incorporating superparamagnetic nanoparticles (SPIONs) within the colloidosome-forming shell it is possible to design microcapsules with responsiveness to an external magnetic field (Figure 1-a). After colloidosome-loading with active agents this physical property may be utilized for hyperthermia cancer treatment or drug-targeting. Second, fluorescently labeled nanoparticles (FLNPs) were incorporated within colloidosomes (Figure 1-b) for the purpose of cell tracking or in order to study their interactions with cellular subunits. The combined assembly of multifunctional submicron colloidosomes from SPIONs and FLNPs (Figure 1-c) was achieved via the formation of Pickering emulsions. Next to assessing the functionality of the colloidosomes, the capsules were thoroughly characterized using electron microscopy, DLS, and interfacial shear rheology.

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## **Hierarchical Series of Ligands with Controlled HLB for Different Types of Sensory Systems**

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To solve challenging problems of environmental and health monitoring, the development of highly selective and sensitive sensory systems for detection of metal ions in aqueous media is required. With this aim in mind, hierarchical series of modular receptors with controlled hydrophilic-lipophilic balance (HLB) were developed and their sensory properties were implemented in colorimetric and film systems of different types. Amphiphilic ligands of these hierarchical series are composed of 9,10-anthraquinone signalling moiety linked *via* amino groups to a receptor subunit bearing amide and diethoxyphosphoryl groups and decorated by two hydrophobic alkoxy chains. Binding of environmentally relevant metal ions by these amphiphilic chromoionophores with variable HLB were studied in solution, monolayers, Langmuir-Blodgett films, polymer films and test strips using electron absorption spectroscopy, surface balance technique, *in situ* fiber-optic absorption-reflection spectroscopy, surface plasmon resonance spectroscopy (SPRS) and scanning electron microscopy. Molecular architecture of studied ligands provides an appropriate orientation of the planar anthraquinone moiety at the interface that allows to prevent  $\pi$  stacking of the molecules in the films. Conservative behavior of these amphiphilic modular compounds having bulky polar moieties and a significantly different length of alkyl chains in sensory monolayers was observed. Kinetic and thermodynamic parameters of the complexation of various metal ions by ligand monolayers immobilized onto a gold support were calculated using SPR-sensorgrams. The efficiency of this design strategy was demonstrated by the development of highly sensitive sensory systems for detection of mercury and copper ions in aqueous media.

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***Invited Lecture:***  
**Nanomaterials for Functional and 3D Printing**

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Nanomaterials have unique properties which enables their utilization in functional printing and coatings. Our research is focused on developing methods for preparation and formulations of nanomaterials, and utilization of these materials as "inks" and "paints" for functional coatings and printed electronics. The formation and application of conductive inkjet inks composed of silver, copper, copper@silver and carbon nanotubes will be reported. These inks address a major challenge in fabrication of plastic electronics devices, the printing at sufficiently low temperatures which will not damage the polymeric substrates. Our recent discoveries of several routes for achieving high conductivity even at room temperature will we discussed. These methods are based on various concepts of colloid and interface chemistry, such as coalescence and wetting processes that are observed in "coffee ring effect". While combining the low sintering temperatures concepts with self assembly processes, we fabricate transparent conductive films that are suitable for optoelectronic devices (such as smartphone touchscreens) and **3D** conductive structures. Some applications will be demonstrated in the fields of inkjet printed solar cells, smart windows, paper RFID antennas, touch screens, light sensors and plastic electroluminescent devices.

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### **Cubosomes and Hexosomes in Theranostic Nanomedicine**

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Application of nanotechnology to medicine offers a versatile approach for the design and the development of new multi-functional drug delivery systems where imaging probes, drugs, and targeting agents can be combined and applied as therapeutic/diagnostic (theranostic) tools. Furthermore, this application requires the development of biocompatible and non-toxic systems with tunable properties. In this context, lipid-based nanoparticles seem to be flexible platforms, since they can be personalized depending on their application.

Here, two types of nanoparticles based on a biocompatible lipid (monoolein), respectively known as cubosomes and hexosomes, are proposed as theranostic platforms for cancer treatment. Both these nanoparticles show high mechanical rigidity and structural stability and, because of their intrinsic nanostructure, can be loaded with hydrophobic or hydrophilic cargos. It will be shown that cubosomes and hexosomes can effectively be loaded with anticancer drugs, UV-visible or NIR emitting fluorophores, while simultaneously conjugated with cancer cells-targeting ligands. Their living cells imaging skills and addressing abilities toward HeLa cells will be also presented.

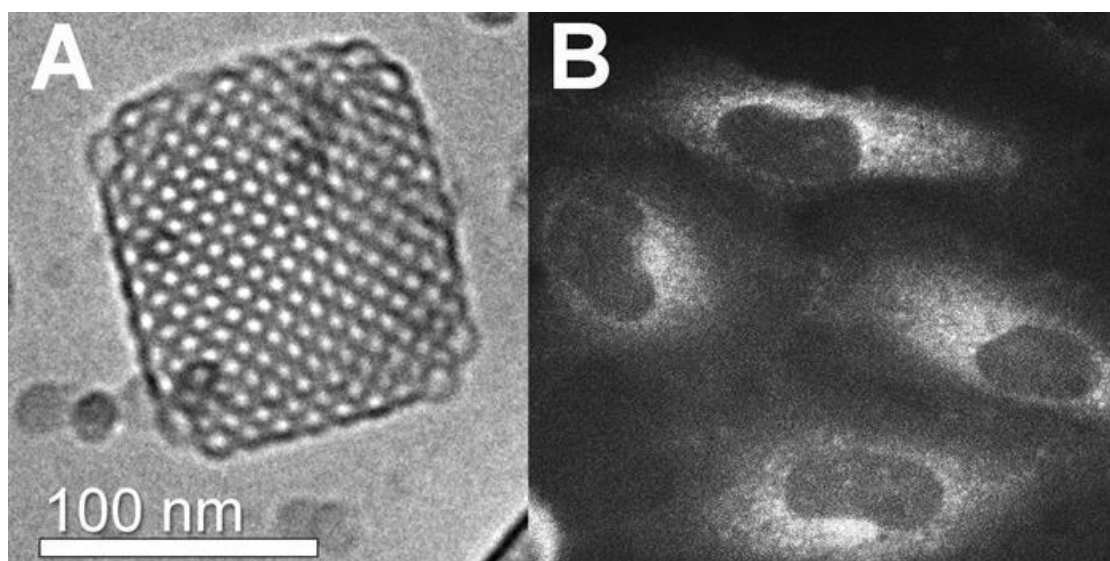


Figure. (A) Cubosome nanoparticle loaded with quercetin and prepared with dansyl-conjugated F108 Pluronic. (B) Fluorescence image of viable 3T3 fibroblast cells after treatment with cubosomes loaded with hydrophobically modified fluorescein.

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S. Murgia, S. Bonacchi, A. M. Falchi, S. Lampis, V. Lippolis, V. Meli, M. Monduzzi, L. Prodi, J. Schmidt, Y. Talmon, C. Caltagirone, *Langmuir*, 2013, 29, 6673

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### **Block Copolymer Aggregates in Planar Multilayer Assemblies**

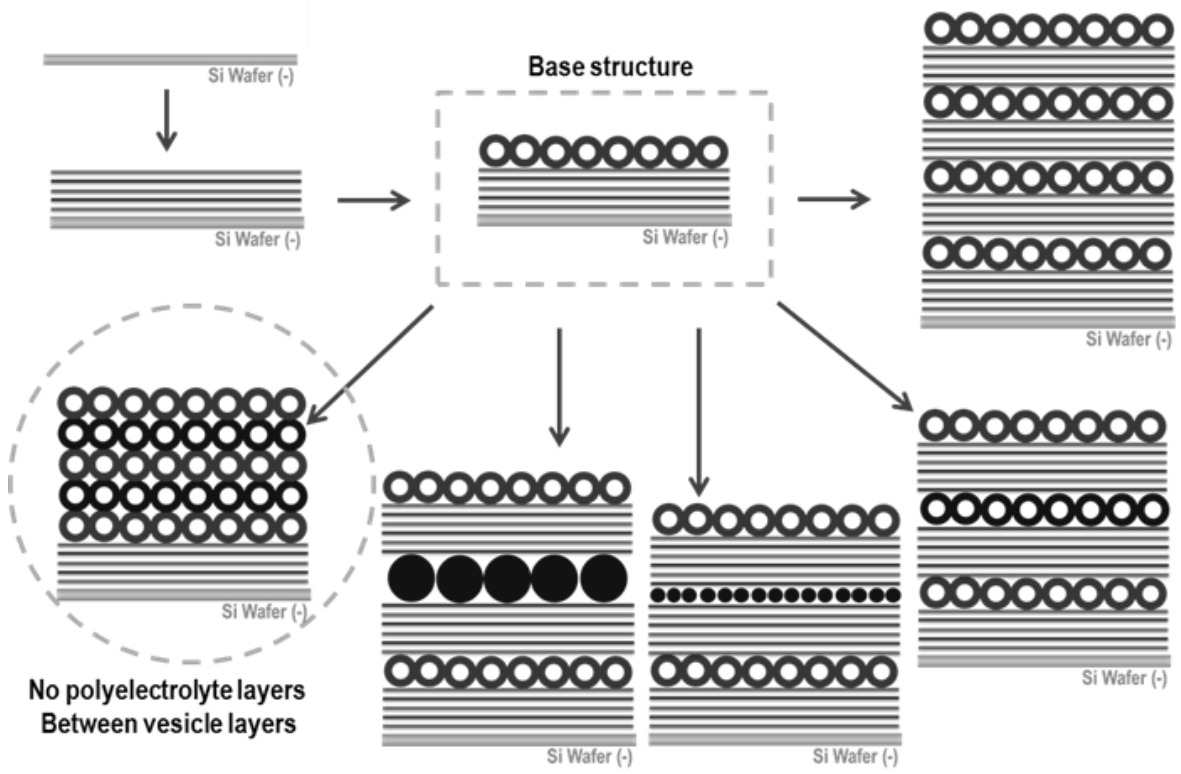
Renata Vyhnanekova<sup>1</sup>, Lin Xiao<sup>2</sup>, Miloslav Sailer<sup>1</sup>, Guang Yang<sup>2</sup>,  
Christopher J. Barrett<sup>1</sup>, Adi Eisenberg<sup>1</sup>

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Planar multilayer structures were designed and prepared from various combinations of sequentially deposited layers of individual polyelectrolyte (PE) chains and layers of self-assembled block copolymer aggregates (vesicles, micelles, etc.), and their properties were investigated. The aggregates consist of negatively or positively charged corona chains on a non-ionic core (hollow in case of vesicles), while the PE multilayers contain alternating polyanionic and polycationic chains, deposited on silicon wafers. Two types of layer-by-layer (LbL) structures were studied: One consists of individual layers of identical aggregates sandwiched between PE multilayers; the aggregates can all be of the same type or, sequential particle layers can consist of aggregates of different morphologies or compositions. The second is composed of layers of individual aggregates of various morphologies and of different corona chain charges, deposited on top of each other without intermediate PE multilayers. Strong interactions between the successive layers are achieved mainly by electrostatic attraction between the oppositely charged layers. The planar LbL multilayers could, potentially, be used as carriers for multiple functional components with each aggregate layer loaded with hydrophobic (in the core of the micelles, LCMs or vesicle walls) or hydrophilic functional molecules (in the vesicular cavities). The overall thickness of such planar LbL multilayers can be controlled precisely and can vary from tens of nm to several  $\mu\text{m}$  depending on the number of layers, the sizes of the aggregates and the complexity of the structure.





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**A Novel Thermodynamic Sensor for the Detection of Mobile Counter Ions**

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To measure the mobile counter ion concentration produced by charged colloids or interfaces, we have developed a new alternative in the form of a charge sensor that directly probes the ratio of charge  $z$  to mass  $m$  of charged species in solution. The sensor consists of a small salt solution confinement separated by a membrane interface from a bulk of suspended charge carriers. The sensor state emerges as a limiting case of the equilibrium salt imbalance, and the ensuing osmotic pressure difference, between arbitrary salt and suspension volumes. The thermodynamic principles underlying the sensor will be explained, followed by an account of the design and construction of the sensor, together with illustrative experiments on solutions of poly-dextrane sulphate and bovine serum albumin. The thermodynamic  $z/m$  determination appears to be accurate and reproducible, and is a promising alternative for kinetic methods such as electrophoresis and electroacoustics that are hampered by turbidity or concentration effects.

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## **Adsorption and Surface Forces Study in Polyelectrolyte Solutions: Theoretical Predictions and Experimental Measurements**

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This work utilizes a combination of theory and experiments to explore adsorption on (ellipsometry) and forces (AFM) between silica surfaces, immersed in solutions containing highly charged cationic polyelectrolytes. We investigate salt responses, as well as how adsorption and surface interactions depend upon the average degree of polymerization, and polymer type. For all kinds of polyelectrolytes we studied, at low concentrations of simple salt, the adsorption increases with ionic strength, reaching a maximum at intermediate levels (about 200 mM). The adsorption then drops but retains a finite level even at very high salt concentrations, indicating the presence of nonelectrostatic contributions to the adsorption. The adsorption of polymer with shorter chain length increases more slowly in lower salt region but drops stronger in higher salt region comparing with longer chain polymer. We shall demonstrate that our recently developed correlation corrected classical density functional theory prediction captures the overall adsorption behaviours, even under the assumption that the adsorption is of purely electrostatic origin, since a silica surface usually carries a relatively high charge at pH 9, which means we have specifically chosen to investigate adsorption under conditions where electrostatics dominate the interactions. However, the short-ranged non-electrostatic surface affinity was also estimated by matching predicted and experimental slopes of adsorption curves at high ionic strength. Additionally, since the surface charge density of silica varies with different salt concentration, the titration surface effects were also considered in the theoretical treatment. This leads to a quantitative improvement, as compared with experimental data, especially at low salt. Given these estimates for the nonelectrostatic part and titration response, experimental adsorption data are essentially captured with quantitative accuracy by the classical density functional theory.

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## **A Superfluorinated Probe for Highly Sensitive *In Vivo* <sup>19</sup>F-MRI**

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Alfonso Mastropietro<sup>4</sup>, Chiara Cordiglieri<sup>5</sup>, Ileana Zucca<sup>4</sup>,  
Maria Grazia Bruzzone<sup>4</sup>, Fulvio Baggi<sup>5</sup>, Metrangolo Pierangelo<sup>3</sup>,  
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With his high natural abundance, characteristic resonance properties, and its negligible presence in the human body, fluorine is a perfect candidate for *in vivo* MRI. [1] In the past ten years plenty of studies have been published on the use of <sup>19</sup>F-MRI in the diagnosis and treatment of various diseases. [2] Several fluorous reporter agents have been used, mostly consisting of liquid perfluorocarbons (PFC) or perfluoropolyethers (PFPE) administered as nano formulations. In this communication we wish to report the synthesis and full characterization of a novel <sup>19</sup>F-MRI reporter consisting of a single highly fluorinated symmetrical molecule and its facile and scalable formulation in water, which yields a stable and monodisperse nanoemulsion of a mean particle size of 150-210 nm, allowing for the dispersion in water of up to 100 mg/ml of the reporter. The unique structure of this molecule results in a single, very intense <sup>19</sup>F-NMR peak, which ensures facile identification of the reporter and avoids artefacts formation, particularly in MRI experiments. Biocompatibility was evaluated *in vitro* on two different cell cultures showing no cytotoxicity and excellent survival rate. Finally both *in vitro* and *in vivo* <sup>19</sup>F-MRI experiments showed very low detection limits, short acquisition time, and good detectability *in vivo*, even for small number of cells. These promising results may pave the way to different modifications of the nanoemulsion, allowing several *in vivo* applications of the reporter, which are under current investigation in our laboratory.

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## **Dynamic Wetting of Surfactant Solutions - Coupling to the Flow Field**

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Wetting and dewetting play an important role in the natural environment and in many technical applications, e.g. cleaning surfaces. The wetting behavior of a single component liquid has been investigated in many studies. The wetting characteristics of surfactant solutions has not been in the focus of experimental attached less attention. Some efforts were made to gain deeper insight of the physical mechanisms, e.g. it was shown that there is a strong influence of the surfactant on the dynamic contact angle.

The contact angle decrease with increasing surfactant concentration. The effect on the dynamic contact angle is much stronger than expected from the changed in surface tension. Simple estimates show that the driving mechanism is most probably due to Marangoni stresses along the free liquid-air interface. These stresses couple to the hydrodynamic flow and induce changes in the flow profile close to the contact line. The range of this region is typically 100  $\mu\text{m}$ . We present results of the dynamic contact angle as a function of receding velocity and surfactant concentration and correlate them to the measured changes in the flow field close to the contact line.

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## Functional Surface Micro-Patterns by Dewetting of Polymer Thin Films

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The dewetting of polymer thin films on solid substrates represents a versatile and robust process to produce surface micro-patterns with controlled topography and surface chemistry. In this work, we use complementary approaches to engineer both the ordering and the surface chemistry of the dewetting patterns. The produced micro-patterned surfaces could be used in biological applications requiring spatially localized features of controlled surface chemistry, e.g. proteomics, single cell studies and biosensors.

Spatially ordered dewetting patterns were obtained by two means: (i) by pre-stamping the substrates with micro-contact printing, to drive the dewetting of polystyrene thin films within specific regions of the substrate (Figure 1a);<sup>1</sup> and (ii) by using two-dimensional colloidal crystals as patterning templates (Figure 1b). Surface patterns obtained by dewetting of polymer thin films were employed to control the positioning of proteins on the micro scale, by selective adsorption of proteins on specific regions of the substrate (Figure 1c).<sup>2</sup> The simplicity of the surface patterning and functionalization approaches gives rise to possible applications in cell co-cultures for tissue engineering.

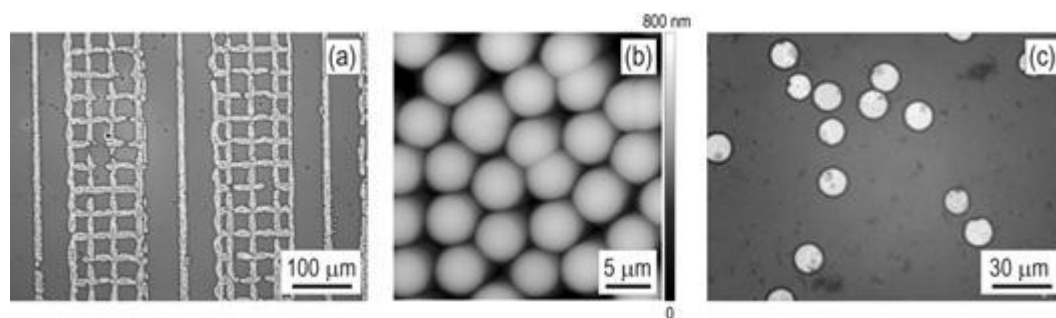


Figure 1. (a) Spatially ordered surface pattern by polymer dewetting on micro-contact printed substrate. (b) Two-dimensional colloidal crystal on a polymer film. (c) Protein micro-patterning by selective adsorption on dewetting patterns.

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## **Capillary Penetration Based Rapid Test for Flying Oil Quality Determination**

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This work presents a novel apparatus and method for determining frying oil quality based on the measurement of the rate of spontaneous capillary penetration in porous media. The rate of liquid penetration of a wetting liquid in a porous medium having pores of capillary dimensions depends on the liquid and porous medium properties (liquid viscosity and surface tension, liquid/solid contact angle, pore sizes and tortuosity of the porous medium). Furthermore, and depending on penetration conditions, the penetration rate can be affected also by gravity, inertia, spreading pressure and other variables. The measurement of capillary penetration rate has been used in the past for the determination of contact angles and/or pore radii in porous media. To our knowledge, the present method is the first effort to use the measurement of capillary penetration rate for the determination of liquid properties and particularly frying oil quality. Frying in the food industry/catering sector involves heating the oil for several days in the presence of food. This process results in serious quality degradation with negative effects for human health. The major groups of compounds formed during frying are polar and polymer compounds which change the oil's surface tension and viscosity. A rapid test is being developed measuring frying oil quality taking advantage of the changes in frying oil properties and based on the measurement of capillary penetration rate. A prototype design and results on model liquids and oils heated/fried under different conditions are presented proving the capabilities of the method.

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## **Swelling Enhancement of Polyelectrolyte Brushes Induced by External Ions**

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It has been observed previously that, when polyelectrolyte brushes are exposed to external salt solution, it becomes thinner when the salt level is high enough. Before the salt concentration gets to that limit, an enhanced swelling process is discovered in this study with a few polyelectrolyte brush systems, including sodium polystyrene sulfonate (PSSNa), poly([2-(methacryloyloxy)ethyl] trimethylammonium chloride) (PMETAC) and potassium poly(3-sulfopropyl methacrylate) (PSPMA) with different molecular weight and grafting density, by combination of methods including ellipsometry, quartz crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM). The swelling enhancement is expressed by the thickening of the brush layer, accompanied by the decrease of refractive index, the increase of the amount of solvent inside the brushes and the increase of the retardation time. A scenario is proposed as that, when the counterions penetrate into the brushes driven by the external salt ions, they disrupt and break up the previously formed multiplets due to the dipole-dipole interaction by the ion-pairs on the polymer chain. The process results in the release of the bound segments and the stretching of the polymer chains.

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***Invited Lecture:***

**Droplet Spreading over a Soft Substrate: Finite Element Method Coupled with Lubrication Approximation**

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Sessile liquid droplets deposited on soft substrates may cause the substrate deformation and affect the apparent contact angle as well as the spreading dynamics [1-3].

One approach for modelling of these phenomena is a solution of elasticity problem in an infinite half-space under the action of capillary pressure and the concentrated surface tension force applied at the three-phase contact line [4]. This approach requires a definition of a small artificial width, over which the surface tension force is distributed. To avoid this, the concentrated surface tension force has been replaced by a distributed traction based on the disjoining pressure concept [5].

In the present work, dynamic spreading of a droplet over a soft substrate is described in the framework of the disjoining pressure concept. A Finite Element Method for elasticity problem in a substrate is coupled with lubrication approximation for modelling of droplet spreading. The chosen form of disjoining pressure allows an independent definition of contact angle and the thickness of adsorbed layer. Parameter studies are performed to quantify the influence of mechanical properties and size of the substrate, surface tension of the liquid and contact angle on the substrate deformation and spreading dynamics.

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## **Interplay Between Aggregate Formation and Viscosity Increase in Concentrated Colloidal Systems**

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The self-assembly of colloidal particles has been widely addressed in the literature due to its relevance in various systems such as paints, ceramics, waste water, food products or pharmaceuticals. The Smoluchowski's equation has provided a basis for the description of the kinetics of aggregation of colloidal particles under diffusing limited conditions. Nevertheless, its application is restricted to dilute conditions, where several key assumptions are justified. Among others, the viscosity of the dispersion is assumed to be close to the solvent viscosity. However, the viscosity significantly rises upon an increase in particle concentration and upon aggregate formation, which then tends to decrease the aggregation rate.

In this work, we propose a correction to the conventional diffusion-limited aggregation kernel which accounts for the viscosity effects arising in concentrated colloidal systems. First, by means of computer simulations and theoretical arguments, we derive an expression for the diffusion coefficient of a tracer particle immersed in a concentrated dispersion of hard sphere particles. We investigate how the diffusion coefficient of the tracer particle depends on the host volume fraction and on the size ratio of tracer and host particles. The results are then interpreted in terms of an effective size-dependent viscosity which is experienced by the tracer particle: while sufficiently large tracer particles experience the macroscopic viscosity of the colloidal dispersion, small tracer particles rather experience the solvent viscosity. Finally, we introduce this size-dependent viscosity in the aggregation kernel and perform Population Balance Equations simulations to quantify the impact of a viscosity increase on the kinetics of aggregation and on the particle size distribution.

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## **Molecular Exchange Kinetics in a Series of Well-defined n-Alkane-PEO Micelles in Water as Studied by TR-SANS**

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We present the equilibrium chain exchange kinetics in spherical micelles formed by n-alkane-PEO<sub>x</sub> (C<sub>n</sub>H<sub>2n+1</sub>-PEO<sub>x</sub> with n = 18, 21, 24, 27, 30 and x = 5, 10, 20, 40 kg/mol) block copolymers in aqueous solution. Due to the very well-defined system we could systematically study the effect of polymer composition on the molecular exchange kinetics. To access the kinetics we applied a sophisticated contrast variation technique by using time-resolved small-angle neutron scattering (TR-SANS) [1,2,3].

In our study, it was found that the exchange process dramatically depends on the alkane chain length, while the molecular exchange for C18-PEO<sub>5</sub> is too fast, C30-PEO<sub>5</sub>, is too slow to be measured. We will present kinetic results of C<sub>n</sub>-PEO<sub>5</sub> with n= 21, 24, 27 and 28. As expected from theories [4], we find a first-order kinetic process characterized by a single-exponential relaxation function. From temperature dependent measurements we deduced the activation energies for such thermal activated kinetic processes. Furthermore, we show that the relaxation is independent of micelle concentration in the dilute limit, supporting that single-unimer exchange is the dominant kinetic mechanism. Very interestingly, the exchange slows down with increasing PEO chain length.

In our presentation a detailed description of the experiment will be given including a thorough discussion of the main results.

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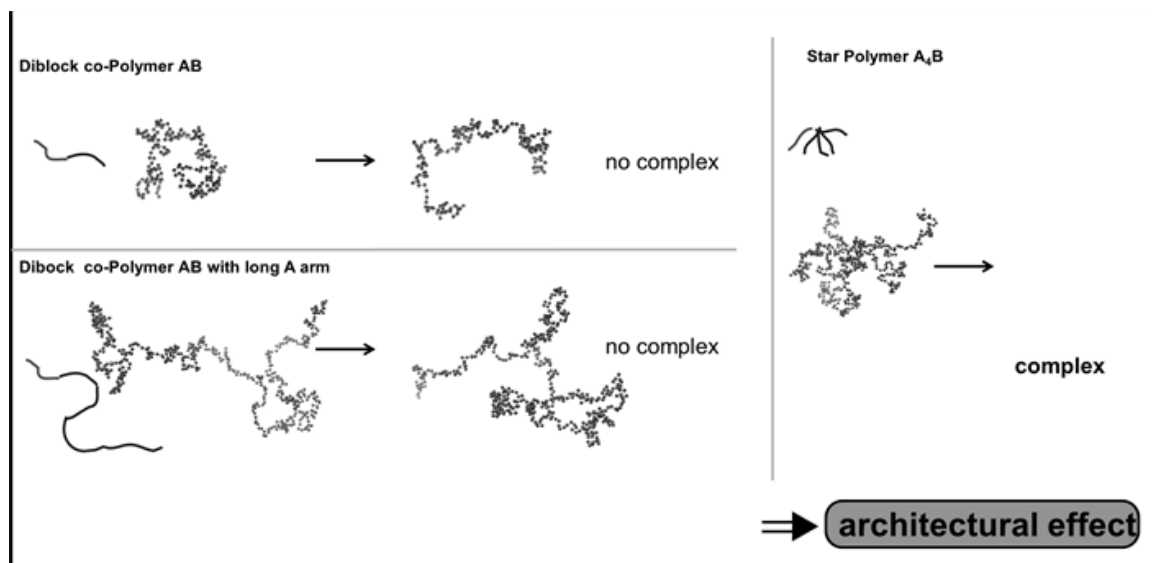
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## Architectural Effects on the Internal Complexation within Star Polymers: Experiment and Simulation

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An effect of local mutual segment density on the complexing behavior of poly(propylene oxide) (PPO) and poly(dimethylaminoethyl methacrylate) (PDMAEMA) was found experimentally.[1] We investigated linear block-copolymers as well as miktoarm star polymers of the two components. A complexation of the PPO chain in the miktoarm stars was found for conditions under which the linear polymer is not complexed.

This architectural effect was investigated using a coarse grained bead spring model for the star polymer. The off-lattice Monte Carlo simulations involved star polymers of the type  $AB_n$  ( $n$ : number of B arms) with a Lennard-Jones (L-J) potential between the beads of arm A and of arm B. The influence of the architecture is investigated for potentials ranging from 0 to 3.0 kJ/mol comparing star polymers  $AB_n$  and linear polymers AB. End to end distances, radial distribution functions, numbers of next neighbors as well as the isotropic form factor were extracted. A significant effect of the architecture was found. Complex formation in the star polymers occurs for significantly weaker interaction potentials than in the linear block-copolymers.



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## **What Drives Sequence-Dependent Adsorption of ssDNA on Carbon Nanotubes?**

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Why ssDNA chains with different sequences selectively adsorb on carbon nanotubes (CNTs) of different properties has puzzled experimental and theoretical scientists for over a decade. In our work, we focus on physical aspects of the problem using a coarse-grained model for the ssDNA-CNT system. Our Monte Carlo simulations reveal significant differences in the adsorbed conformations and adsorption thermodynamics of three investigated sequences of guanine (G) and thymine (T):  $G_{12}$ ,  $T_{12}$ , and  $(GT)_6$ . The competition between base-base and base-nanotube interactions results in ordered but distinct equilibrium adsorbed conformations in the case of the homopolymer chains, and more disordered conformations for the heteropolymer. More generally, the larger guanine bases show preference to be stacked against the nanotube, while the smaller thymine bases remain stacked with neighboring bases. This frustration leads to the disordered conformations observed in the case of  $(GT)_6$ . It is shown that this competition also leads to greater sensitivity of this sequence towards nanotubes of different diameter compared with the homopolymeric sequences. Our findings confirm and elucidate why heteropolymers are used for selective adsorption of CNTs in experimentation.

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**Shape Transitions in Helical Ribbons – from Seed Pods to Chiral Macromolecules**

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Studying the mechanics of *Bauhinia* seeds pod opening we developed a geometric-mechanical model for elastic ribbons with spontaneous saddle-like curvature. When the width of such ribbons grows beyond a critical value, the ribbons undergo a twist-to-helical transition. Experimental study of this transition, using synthetic sheets and pods valves shows excellent agreement with theoretical predictions.

I will show the geometrical equivalence between the seed pod and some self assembled supramolecular structures of chiral molecules. Based on this equivalence we derive several predictions regarding shape selection and shape evolution in such macromolecules.

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**Brownian Dynamics Simulations on the Orientational Distribution and the Rheological Properties of a Suspension Composed of Disk-Like Hematite Particles**

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We have investigated the orientational distribution and rheological properties of a disk-like hematite particle dispersion by means of Brownian dynamics simulations. The present Brownian dynamics method takes into account the spin Brownian motion about the particle axis in addition to the ordinary translational and rotational Brownian motion [1]. We performed the simulations for the various situations to investigate the influence of the shear rate, the magnetic field strength and the magnetic particle-particle interaction strength on the particle orientational characteristics and the rheological properties. In the situation of a strong applied magnetic field, the particles can freely rotate about the magnetic moment direction together with their magnetic moment aligning along the magnetic field direction, which leads to a linear peak-type orientational distribution. If the shear flow becomes dominant, a single peak-type distribution comes to appear more significantly. This is because column-like clusters come to incline in the direction of the angular velocity vector of a simple shear flow under a strong shear flow situation. Since the magnetic moment is more strongly restricted in the magnetic field direction with increasing field strength, the viscosity due to the magnetic properties of the particles increases more significantly. An increase in the magnetic particle-particle interaction strength leads to a decrease in the viscosity. Unless the regime of aggregation structures changes, the viscosity monotonously decreases with increasing Peclet number.

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## **Coalescence Behavior of Sessile Drops with Reacting Liquids: Precipitation Morphologies**

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Unexpectedly, sessile drops of completely miscible liquids do not always coalesce immediately but can remain separated temporarily. This “non-coalescence” behavior is due to a Marangoni flow caused by the surface tension difference ( $\Delta\gamma$ ) between the liquids<sup>[1],[2],[3]</sup>. When the two liquids contain reactants e.g., leading to precipitates, the drop coalescence becomes more complicated. Drop coalescence is interesting not only for fundamental aspects, but is also relevant technologically, for instance in microfluidics and chemical engineering<sup>[4]</sup>.

We study a model reaction, the cerium oxalate precipitation during coalescence of drops of water/propanediol mixtures containing oxalic acid and cerium nitrate. We vary independently the reactant concentrations and  $\Delta\gamma$ , to adjust the advection rates. We analyzed the dynamics and the precipitate morphologies by imaging and diffraction methods. In one of the identified regimes, the precipitation leads to patterns, which correspond to alternating precipitates densities and morphologies. Here we analyze the underlying mechanisms leading to the precipitation scenarios.



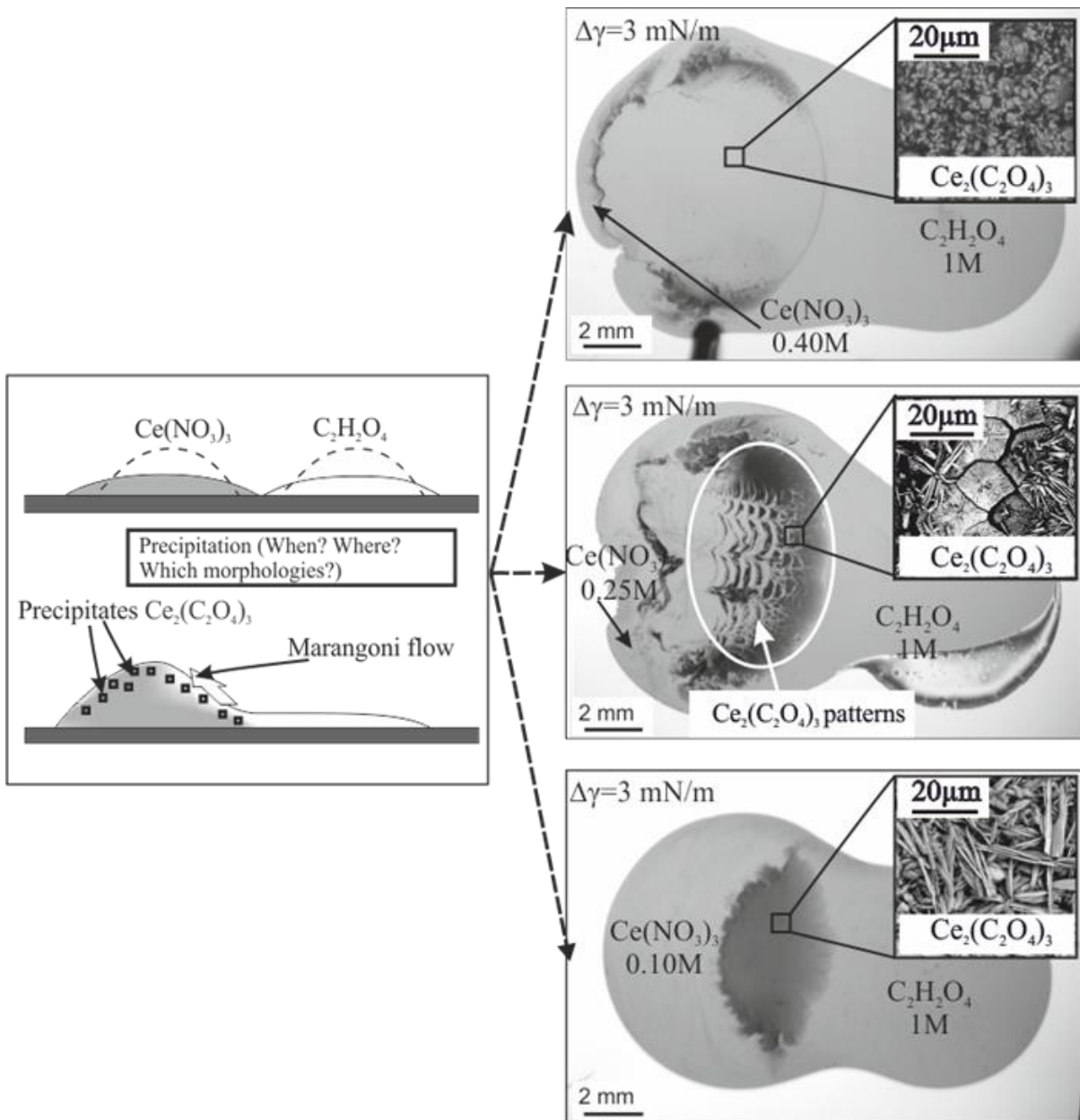


Figure 1: Left: Side view sketches. Right: Top view image of drops containing reagents precipitating after coalescence. Only the cerium nitrate concentrations vary. (Inset: SEM images of the precipitates). At intermediate  $\text{Ce}(\text{NO}_3)_3$  concentrations, intriguing patterns are observed.

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## **The Modification of Multilayer Polyelectrolyte Coatings for Biomedical Applications**

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Diagnostic devices and a variety of biomedical implants are used in direct contact with biological fluids that creates a number of problems. One of the most significant is the process of biofouling, i.e. the unwanted adsorption of proteins, occurring on the surfaces exposed to solutions containing biological material. Therefore, the development of the "antifouling" coatings protecting against non-specific protein adsorption, bacteria and fungi colonization are an important area of research within a broader field of biointerface science. Immobilization of neutral hydrophilic polymers (e.g. poly(ethylene glycol) (PEG)) at surfaces is one of the accepted methods to reduce non-specific adsorption of proteins. On the other hand, silver and/or copper containing materials and coatings with antimicrobial activity find applications: in medicine to reduce infections in hospitals, in burn treatment as well as to prevent bacteria and fungi colonization on prostheses, catheters, vascular grafts, dental materials. One goal of the work was to explore the method of direct immobilization of PEG layer to reduce/eliminate non-specific adsorption of proteins at surface of polyelectrolyte multilayer thin films. Synthesized copolymers of poly(glutamic acid) or poly(L-lysine) with grafted PEG chains with various grafting ratio and various chain lengths, were used for that modification by formation of the external layer of films. The biofouling process was investigated by studying the adsorption of different proteins, e.g. HSA, using Quartz Crystal Microbalance and fluorescent methods. Apart from polyelectrolytes negatively charged silver or copper nanoparticles were used for the multilayers construction, which led to the formation of nanocomposite films. It was found that nanocomposite films have antimicrobial properties, which makes them very interesting for a number of practical application e.g. prevention of microbial colonization on treated surfaces.

### Acknowledgements:

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## **Microemulsions Adjacent to Planar Walls**

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Microemulsions display a higher degree of order at planar hydrophilic walls. The oriented lamellae, furthermore, have three times faster relaxations compared to the bicontinuous bulk structure. Grazing incidence neutron scattering techniques were employed to observe the structure and dynamics (PRE 83, 030401 (2011) & PRE 85, 041408 (2012)). By staying below the critical angle of total reflection an evanescent (tunneling) wave allowed for highlighting near surface layers of varying depth. Especially, the depth resolved dynamics using neutron spin echo spectroscopy have been obtained for the first time in this way. Amphiphilic polymers are the most promising additives in microemulsions since a dramatic increase of the surfactant efficiency usually is obtained (PRE 89, 042303 (2014)). For many applications, the impact of the polymer on the near surface functionality of the microemulsion is highly important. The materials to be cleaned usually appear as huge interfaces, for instance in the soil cleaning. The considered diblock copolymer showed enrichment in the near surface region and the dynamics are slowed down. So the viscosity effect of the polymer is amplified at the surface. We speculate that the exposure time of the fluid is increased in a rinsing process. The attraction of larger molecules by the confinement could also explain better binding of receptors of immune cells at hard vessel walls.

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### **Evaporation of Chemically Modified Nanofluid Droplets**

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Nanofluids are suspensions of nanoparticles with specific interfacial properties that can be tuned by the addition of surface active molecules. Due to the presence of nanoparticles, nanofluids raise fundamental questions when investigating their properties. One still challenging problem in this context is the description of the overall evaporation kinetics of modified nanofluid droplets when deposited on solid substrates. In this work, droplets consist in a mixture of 15 nm diameter silica nanoparticles ( $\text{SiO}_2$ ) modified by a surfactant (CTAB). When surfactant free, nanoparticles are soluble in water up to 300 g/L. For large values of CTAB concentrations, they become hydrophobic and change the nanofluid solid/liquid/air interfacial properties. The considered droplets have approximately 1.4  $\mu\text{L}$  volume and are deposited on a copper substrate. Due to their small size, they appear initially as spherical caps. Their evolution is studied under controlled temperature ( $T=22\pm 1^\circ\text{C}$ ) and relative humidity ( $40\pm 2\%$ ) conditions with an optical microscope. For all the experiments, the initial height (resp. contact line diameter) is such that  $h=0.8\pm 0.1$  mm (resp.  $L=2.0\pm 0.2$  mm). For a given CTAB concentration, the evaporation time is shown to be weakly dependent of the nanoparticles concentration as long as  $[\text{SiO}_2] \leq 20$  g/L. This indicates that the addition of a low amount of nanoparticles does not modify significantly the evaporative flows. Conversely, for a given  $\text{SiO}_2$  concentration, evaporation becomes faster when increasing [CTAB]. Finally a critical mixing ratio for which evaporation is the fastest is evidenced.

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**Field-Directed Self-Assembly in Soft Dipolar Fluids**

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Anand Yethiraj<sup>2</sup>, Peter Schurtenberger<sup>1</sup>

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We use ionic poly(N-isopropylacrylamide) (PNIPAM) microgels as a model system to study interactions in soft colloidal systems. Due to the intrinsic and tuneable softness of the particles they are ideally suited to study the complex phase behavior found for soft particles [1]. Subjecting the particles to an alternating electric field results in an additional dipolar contribution to the interaction potential, which strongly depends on the strength and frequency of the field. Here we describe the new phases that emerge with increasing dipolar interactions (Fig. 1) [2].

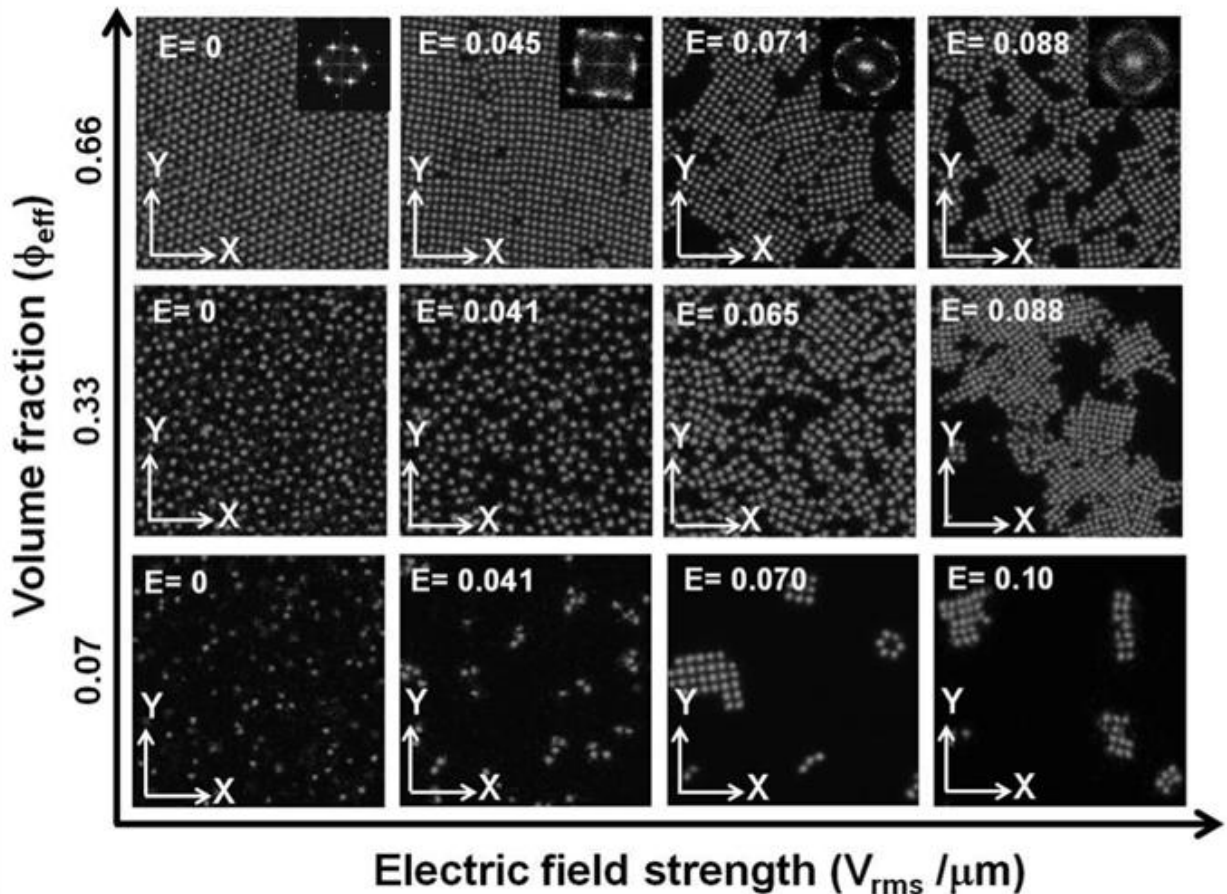


Figure 1. Field induced structures monitored in CLSM. We use a combination of complementary techniques such as confocal laser scanning microscopy (CLSM) and light, neutron and x-ray scattering to monitor and understand the various equilibrium and non-equilibrium transitions. We show in particular that the combination of SANS using the so-called zero average contrast method, SAXS and CLSM allows us for the first time to disentangle interparticle correlation effects due to superlattice formation and changes of the particle size and shape as a function of an increasing dipolar attraction.

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[2] S. Nöjd, P. S. Mohanty, P. Bagheri, A. Yethiraj and P. Schurtenberger, *Soft Matter*, 9 (2013)

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***Invited Lecture:***  
**Who Ordered These Fluid Nanoparticle Suspensions?**

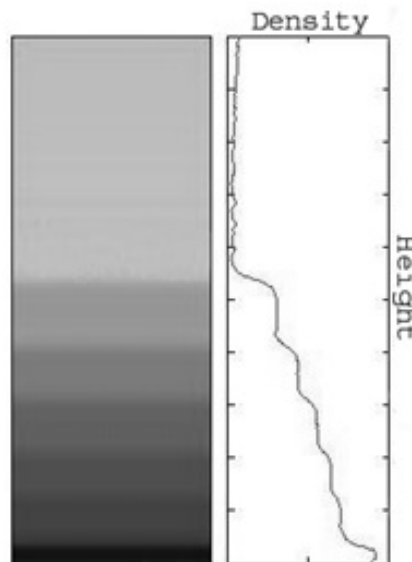
Eli Sloutskin<sup>1,3</sup>, Alexander V. Butenko<sup>1,3</sup>, Pikhaz Nanikashvili<sup>2,3</sup>,  
David Zitoun<sup>2,3</sup>

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Sedimentation of nanoparticles is common in science and technology, yet the dynamics of sedimentation may sometimes be unexpected. We demonstrate spontaneous ordering of sedimenting nanoparticles into well defined layers of constant number density; the corresponding density profiles thus adopt a staircase-like appearance (see Figure).



Similar effects have been observed in micron-sized colloids back in 1884. However, the physical mechanism of these phenomena remained controversial, due to their notorious sensitivity to tiny temperature gradients, such as induced by the radiated body heat of the experimenter. The layering effect in nanoparticles appears to be much more robust, which allowed the critical conditions for the onset of layering to be measured, elucidating the physics of this spectacular phenomenon[1].

In particular, we demonstrate that the layering, breaking the translational symmetry within the sediments, is induced by particle polydispersity and transverse temperature gradients. These archetypal sources of noise, usually maximizing the disorder, are responsible in our case for the emergence of order; strikingly, similar order-inducing role is believed to be played by noise in formation of zebra stripes and in the morphogenesis. In our suspensions, this order-inducing noise competes with thermal diffusion, giving rise to the observed criticality[1].

The understanding of layering thus achieved opens a wide perspective for development of nanopattern formation technologies and new methods for nanoparticle characterization, as also for deeper understanding of the emergence of order in complex noisy systems.

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**Oral Presentations**  
**Friday, September 12, 2014**

***Laureate of the ECIS-Solvay Prize***  
**Non Classical Nucleation and Crystallization**

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The description of nucleation has been dominated by the classical nucleation theory (CNT) for more than 80 years. However, significant problems exist for the understanding and description of real nucleation or crystallization events using CNT. Most problematic in CNT is certainly the assumption of bulk properties even for the smallest metastable clusters. Instead, it has turned out for  $\text{CaCO}_3$  and several other systems that nucleation can also follow an alternative pathway involving prenucleation clusters, which are thermodynamically stable with respect to the initial ions and are solutes containing some tens of ions. It turned out that for  $\text{CaCO}_3$ , the prenucleation clusters can be understood as dynamic polymers and their formation is entropically driven by release of ion hydration water. Prenucleation clusters even form in undersaturated solution without driving force towards precipitation. The current knowledge about prenucleation clusters will be presented and discussed.

But even beyond the stage of nucleation, crystal growth does not necessarily proceed along the classical mechanism of the addition of atom/ion/molecule building units to the growth sites of a growing crystal. Instead, nanocrystals can self assemble via different mechanisms or crystallize from an amorphous precursor phase to form so called "Mesocrystals". This is an abbreviation for "Mesoscopically structured crystals" and involves the crystallographically aligned superstructure of nanoparticles as a kinetic intermediate. Potential fusion of the already crystallographically aligned nanoparticles after displacement of surface attached stabilizer molecules can lead to crystallographic fusion of the two aligned crystal faces better known as "Oriented Attachment". These processes are known as "Nonclassical Crystallization". Several of these nonclassical mechanisms will be presented and discussed.

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## Dispersed Lipid Liquid Crystalline Nano Particles as Substrate for Lipolytic Enzymes

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We have since over 12 years studied the effect of lipolytic enzymes on lipid liquid crystalline nano-particle structure, including the relation between the lipolytic activity and substrate nano-structure.<sup>1-3</sup> The aim is to provide relevant substrates to monitor and assay the effect of different lipolytic enzymes on these lipid assemblies. This will help to design new vehicles for more efficient and even targeting drug delivery. Well-ordered liquid crystalline nanoparticles (LCNPs) have been used as substrates for lipase to establish the relation between the catalytic activity and the change of structure determined by cryo-TEM and synchrotron SAXD.

We show that the sequence of phases formed are controlled by pH: At pH 8.0 and above bicontinuous Im3m cubic LCNPs, based on monoolein, transform into "sponge"-like assemblies and disordered multilamellar onion-like structures upon exposure to lipase. At pH 7.5 and below lipolysis induced phase transitions of the inner core of the particles, following the sequence Im3m cubic – reversed hexagonal – reversed micellar Fd3m cubic – reversed micelles.

Enzyme catalysed degradation of GDO in cubic micellar (*Fd3m*) nanoparticles of 50/50 (wt%/wt%) soy phosphatidyl choline (SPC)/glycerol dioleate (GDO), the particles retain their morphology. Here the  $I_2$  structure with negative membrane curvature tend to form LC structures of gradually less negative curvature (2D hexagonal, bicontinuous cubic and sponge) before the lamellar phase is formed.

We have also probed the lipase action at the lipid aqueous interface using neutron reflectometry and lipase active and inactive mutants.

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## **Self-Assembled Monolayer of Metal Diisocyanide Complexes on Gold Surface: Application in Selective Catalysis**

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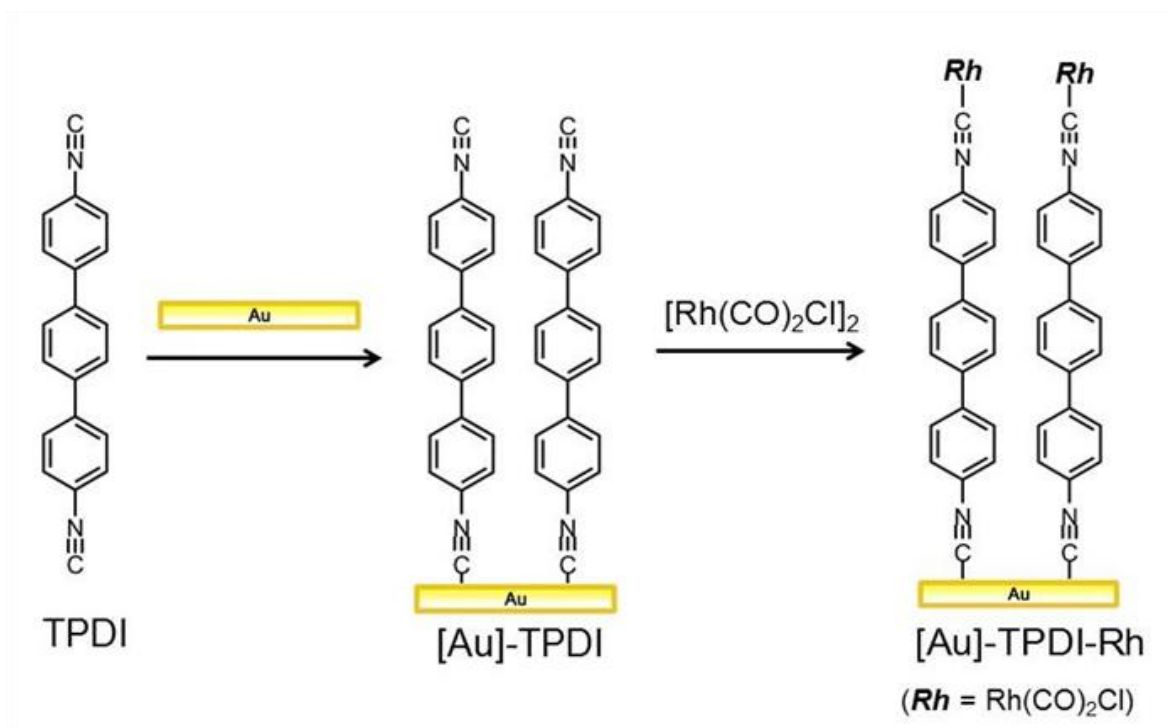
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Self-assembling of organic molecules on surface automatically forms ordered densely packed molecular monolayer. This spontaneous phenomenon can be used as one of the promising low-cost methods to prepare functional materials. The most commonly used system is self-assembled monolayer of alkane thiolate on gold surface, whose application has been expanded to a wide range of functional devices including catalyst. We envisioned utilization of much less studied monolayers, monolayers of isocyanide, for catalyst preparation. We report herein the modification of gold surface with 4,4'-terphenylenediisocyanide (TPDI) as platforms for high turnover and selective Rh-catalyst in 1,4-hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds.

A gold surface evaporated on glass plate was immersed in a  $\text{CHCl}_2$  solution of TPDI to obtain the monolayer of TPDI on Au surface. The successive immersion in a benzene solution of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  gave Rh-immobilized monolayers, **[Au]-TPDI-Rh**. Characterization of thus obtained surfaces was conducted by XPS, IR-RAS and ICP-MS.

The test reactions with 2-cyclohexene-1-one showed that **[Au]-TPDI-Rh** exhibits high selectivity to cyclohexanone over further reduced product, cyclohexanol. The selective 1,4-hydrogenation with **Au-TPDI-Rh** could be applied to a wide variety of  $\alpha,\beta$ -unsaturated carbonyl compounds. Typical catalyst turnover numbers are as high as in a range of 50,000 to 150,000 per Rh atom grafted on the monolayer. The catalyst can be used repeatedly at least five times without obvious deactivation. The monolayer of diisocyanide molecule on gold surface was thus confirmed as a useful platform for selective Rh-catalyzed hydrogenation reaction of  $\alpha,\beta$ -unsaturated carbonyl compounds.



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**Smart Silica-based Ordered Mesoporous Materials to Address Biocatalysis or Nanomedicine Applications: Morphology and Surface Properties Modulation**

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Silica based ordered mesoporous materials (OMMs) have outstanding textural and structural features that make them suitable hosts for bioactive molecules.

Indeed this kind of material can be easily used to immobilize proteins either to produce a biocatalyst or to prepare a drug depot system which provides a highly protective matrix for sensitive drugs such as therapeutic proteins. It is remarkable that the use of OMMs allows for obtaining very stable and reproducible systems. In the Nanomedicine field some applications both as drug delivery and diagnostic systems have recently been reported.

Several OMMs such as SBA-15 or MCM-41 are well known and widely investigated. A variety of different morphologies in terms of long range order or disorder, surface area and pore size dimensions can be produced introducing modifications either in the template preparation (different additives and/or surfactants) or in the choice of the silanizing precursors. Additional surface functionalizations can address the final applications.

Some successful cases will be presented. The case of a lipase immobilized onto SBA-15 via chemical adsorption to obtain a very efficient and re-usable biocatalyst for the production of biodiesel. The release of Lysozyme immobilized via physical adsorption onto different OMMs. Finally the case of SBA-15 and MCM-41 functionalized with Hyaluronic acid to provide silica particles endowed of bioadhesive properties in the perspective of a drug delivery depot system.

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D. Steri, M. Monduzzi, A. Salis - *Microporous Mesoporous Mater.* 170, 164-172, 2013

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## **Carbon Nanosheets from a Hexayne Amphiphile at Room Temperature**

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Two-dimensional (2D) carbon nanostructures, including graphene and carbon nanosheets are of high interest for fundamental studies of the physics of organic electronic materials for novel types of nanocomposites or nanomembranes, as well as for use in capacitors, actuators, and sensors. The direct access to tailored, dispersible materials with controlled surface chemistry, however, is impeded by the typical methods of preparation using either exfoliation techniques or high-energy processes. Here, we report direct access at room temperature to functional carbon nanosheets of uniform thickness. The novel approach is based on the self-assembly and subsequent carbonisation of a hexayne amphiphile at the soft air/water interface. The monolayer has been characterized by X-ray techniques and Infrared spectroscopy. All these experiments confirmed unambiguously the presence of a monolayer of the hexayne amphiphile that comprised a densely packed array with the alkyl chains in an ordered all-trans state. The monolayer exhibited a thickness of 2.6 nm and tilt angles of 62° and 35° for the hexayne and dodecyl segments, respectively. Most importantly, the very tight packing of the reactive hexayne segments leads to a whole series of close carbon-carbon short contacts in a less than 7 Å thick 'carbon precursor' sublayer. Subsequent ultraviolet irradiation of the films resulted in complete carbonisation of the molecular precursors at room temperature to produce sp<sup>2</sup>-rich carbon nanosheets with a carbon microstructure that resembled amorphous carbon materials typically obtained after annealing at temperatures above 800 °C. In this way, we produced mechanically stable and rigid functionalised carbon films that bear similarities to reduced graphene oxide, with a molecularly defined overall thickness of 1.9 nm and lateral dimensions on the order of centimetres that are, presumably, only limited by the dimensions of the Langmuir trough.

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***Invited Lecture:***  
**Carbon-nanotubes Mediated Assembly of Surfactants and Polymers**

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It is becoming evident that the inclusion of nanometric colloids and nanostructures in liquid mixtures of self-assembling surfactants or polymers strongly affects the phase diagram of the host. Nano-inclusions were found to modify the phase boundaries, shift the onset the liquid-liquid phase transition, the onset of micellization, modify the characteristic spacing and symmetries of liquid-crystalline (LC) phases and more. This behavior is fundamentally different from that of micrometric and large colloidal particles with typical diameters in the range of several hundreds of nanometers. I will describe in detail our observations of such behaviors and discuss the suggested origins of the observed behaviors.

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