

Protein particles at water-water interfaces

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Particle-stabilized emulsions, so-called Pickering emulsions, have received considerable interest, due to their outstanding stability against coalescence. Several particles have been used as stabilizers, mostly non-food grade, such as silica particles, but also food compatible particles mainly from polysaccharides. As opposed to polysaccharides, proteins received less attention as particle-stabilizers.

The aim of this project is to demonstrate the use of food-grade proteins, such as the corn protein zein, as an attractive source of particulate material and to investigate their surface activity, in particular at water-water interfaces. Water-water interfaces occur between phase-separated aqueous solutions of incompatible polymers, such as gelatin and dextran, and they are also known as water-in-water emulsions. The most characteristic property of these systems is the ultra-low interfacial tension (a few $\mu\text{N/m}$ or less), compared to the classical oil-in-water emulsions, which makes the adsorption of particles, and hence the emulsion stabilization, a real challenge. However, the stabilization of water-in-water emulsions would be of great commercial interest, since it offers a way to texturize water-based formulations without using fat or oil.

First, zein colloidal particles (of radius of 60-100 nm) are synthesized through the anti-solvent precipitation method and characterized in terms of size, shape and surface charge properties. Then, water-in-water emulsions are prepared, by mixing appropriate quantities of a zein nanoparticle dispersion with aqueous solutions of fish (non-gelling) gelatin and dextran. The resulting emulsions are studied in terms of their phase separation behaviour and stability against coalescence. The use of zein particles in the formation of stable water-in-water Pickering emulsions is investigated as a function of particle size, particle wettability, particle concentration, pH and ionic strength.

Stability of foams and thin films made from pure silicone block-copolymer melts

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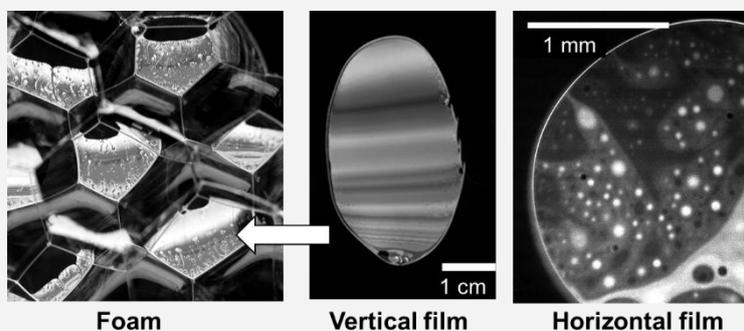
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Because of their broad range of properties, solid polymer foams have become widely used materials in applications such as insulation, seating and cushioning, tissue engineering, catalysis... Each application has specific requirements in terms of foam properties (material, density, cell-size, open versus closed cells etc.). The control of these parameters and the capability to develop new types of polymer foams require that the properties of the initial liquid foam, in particular the key mechanisms involved in its stability, are understood.

Here we present investigations into the development of new types of polymer foams made from amphiphilic silicone block-copolymer melts. To the best of our knowledge, we are the first to report the ability of forming stable foams from a silicone melt whose viscosity is only 2,000 times that of water. To understand this we focus on the study of single vertical and horizontal free-standing films of the polymer melt modeling the thin films separating two bubbles in the liquid foam (Fig 1). These films reach thicknesses below 100 nm while remaining stable for more than 24 hours. We report a number of striking film properties, including the observation of stratification below a critical film thickness. To elucidate our observations we discuss the influence of various parameters such as temperature, pulling velocity or humidity on the film behavior. We use these results together with X-Ray scattering, RMN characterisation, and simple optical observations to discuss the relationship between the molecular structure of the block-copolymer, its organisation at the microscopic scale and the properties that it confers to thin films and foams at the macroscale.



Multiple Light Scattering to characterize emulsions with polymers

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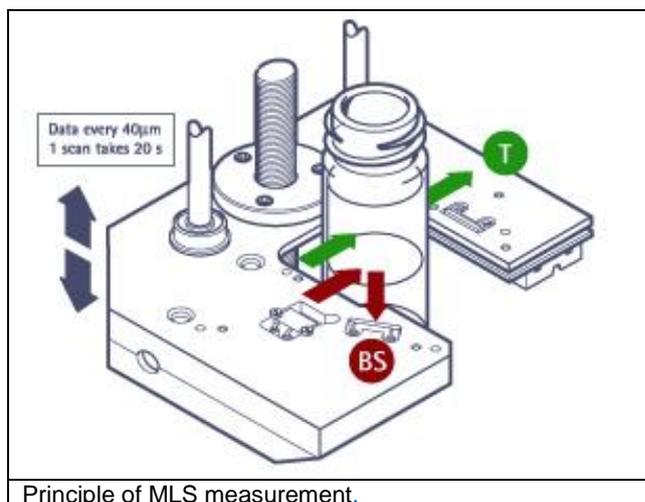
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Polymers are widely used in the industry as a tool to increase the stability. Depending on their concentration, they can act as depletion agents or gel agent. The stability of these systems is driven by the polymers and the structure of the network of droplets and can lead to collapse of the emulsions.

In this work, Multiple Light Scattering device is used to monitor the behaviour of w/o emulsions stabilized with polymers. The heart of the optical scanning analyser is a detection head, which moves up and down along a flat-bottomed cylindrical glass cell (see figure). The detection head is composed of a pulsed near infrared light source (wavelength = 880 nm) and two synchronous detectors. The transmission detector (at 180°) receives the light, which goes through the sample, while the backscattering detector (at 45°) receives the light scattered backward by the sample. The detection head scans the entire height of the sample, acquiring transmission and backscattering data every 40 µm.

We propose a description of the behaviour of o/w emulsions stabilized with different polysaccharides, we will show the advantages of using Multiple Light Scattering (MLS) to monitor their stability and propose a method to predict stability of these emulsions thanks to their size evolution in the first days after preparation.



Ad layers of poly(Lysine)-based copolymers : a versatile strategy to control surface properties in water.

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A simple mean to adjust surfaces properties and colloidal interactions is to grow, or attach, polymer layers on surfaces. Diverse chemistry are generally required to address modification of diverse surfaces (glass, polymers), and preparation of mixed polymer layers remains challenging because it requires to control the surface-density of chemically distinct attachment points. We develop a straightforward method to functionalize anionic surfaces and tailor the density of surface-bound functional moieties with no need for specialized chemistry. It relies on tight spontaneous adsorption of comb-like polycationic derivatives of poly(Lysine) (PLL). PLL grafted with polyethylene oxide (PLL-g-PEG) imparts surfaces with repulsive properties in water, while PLL carrying either reactive PEG strands^{1,2}, or temperature-responsive ones (poly(N-isopropylacrylamide strands, PNIPAM), allow to trigger binding and/or attractive interactions.

We will present two illustrations of surfaces coated with remotely switchable PLL derivatives.

(1) micropatterned glass substrates: Micropatterns are formed by UV-etching of PLL-g-PEG-coated glass, and subsequent coating of the etched regions with PLL-g-PNIPAM polymer. Variation of the deposited fraction of active strands is obtained by coadsorption of the two polymers. Attraction patterns were correlated with collapse of PNIPAM grafts (measured by AFM in water), and capture of Streptavidin-conjugated particles.

(2) colloid dispersions of glass, or polystyrene, particles (diameter 50 nm to 1 micron) endowed with temperature-controlled stability. We studied interparticle aggregation as a function of PNIPAM density in the particle's corona (mixed with PEG strands) providing reversible switch at $32\pm 1^\circ\text{C}$.

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Topic 1- Interfaces, Membranes, Films, Emulsions and Foams

Emulsions stabilised by whey protein microgel particles: towards food-grade Pickering emulsions

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Stabilisation of interfaces by nano/micro particles was first reported more than one century ago and is now also known as “Pickering stabilisation”. A considerable increase in the research activities in this field has been seen over the last decade due to the peculiar behaviour of particles at interfaces and the unique properties they confer to the formulated materials. However, so far much of the fundamental research work has been performed with non-food-grade model particles in order to develop further the concept of Pickering stabilization. Furthermore, adapting it to the constraints of food industry is still a current challenging issue.

In this context, we have investigated a new class of food-grade particles, whey protein microgels, as stabilisers of triglyceride-water emulsions.¹ The sub-micron sized particles stabilized oil-in-water emulsions at wide range of pH and different salinity; both affecting properties of the resulting emulsions. All emulsions creamed but exhibited exceptional resistance to coalescence. A combination of optical microscopy of the drops and spectrophotometry of the resolved aqueous phase allowed us to estimate the interfacial adsorption densities of the particles using the phenomenon of limited coalescence. These findings were supported by direct visualization of drop interfaces using cryo-scanning electron microscopy from which we could deduce different classes of particle arrangement around droplets. In addition, we also discuss herein the correlations found between the properties of the microgels in aqueous dispersion, their organization at interface, and the resulting emulsion characteristics.

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Structural characterization of Histatin 5 in aqueous solution. A combined SAXS and Monte Carlo simulation study

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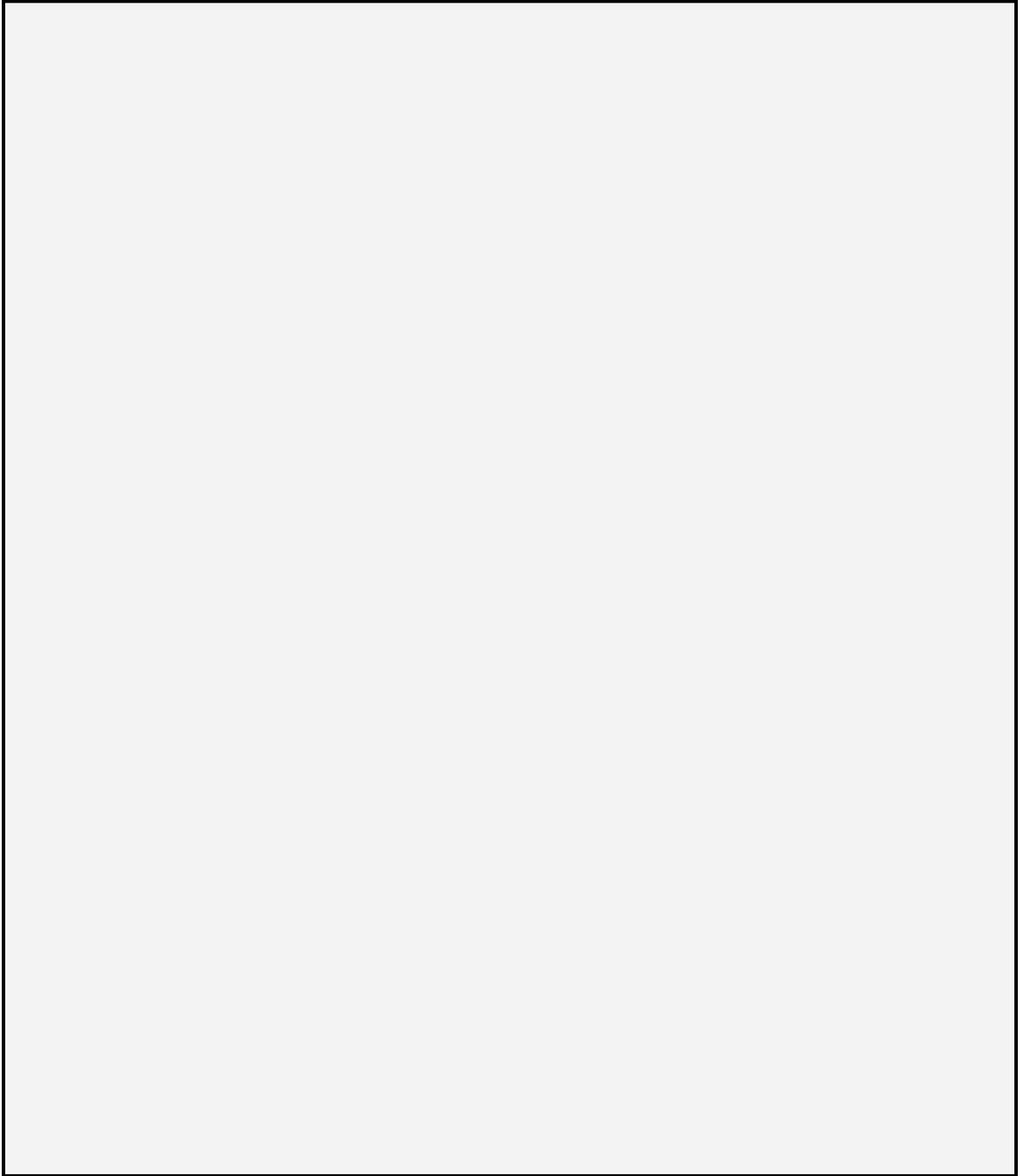
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For more than 30 years, a coarse-grained model based on the primitive model, in combination with Monte Carlo simulations, have been used to model polyelectrolytes and polyampholytes under various conditions. Sometimes this model is also referred to as the bead-necklace model.

Our aim is to apply this model for intrinsically disordered proteins, and verify the simulation results by experiments. As model proteins we are using the salivary protein Histatin 5, which is a 24 AA long peptide, which has a strong fungicidal property[1]. In vitro, it has been found that this fungicidal action is strongly dependent on ionic strength[2, 3]. Conformational properties of Histatin 5 are thought being of importance.

We would like to present results showing good agreement between the scattering curves for Histatin 5 obtained from SAXS and the simulations. At high salt concentration, the protein behaves as a neutral polymer, and at low salt concentration, a repulsive peak is obtained at low q . In the latter regime, it is the net charge of the protein that is of importance for the inter molecular interaction and not the charge distribution. Preliminary results also indicate that the peptide is more stretched out in low pH solutions (in the salivary pH range) as well as in presence of divalent ions such as Zn^{2+} , Mg^{2+} , and Ca^{2+} . This indicates that electrostatic interactions indeed are important for Histatin 5 bulk structure.

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Electrostatic effects in suspensions of hollow spheres

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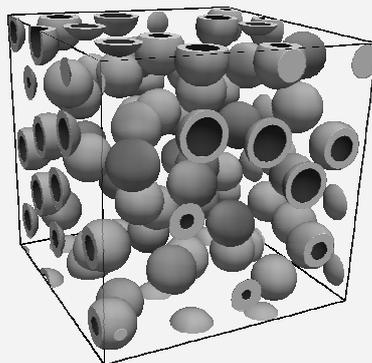
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Nanometric hollow spheres have drawn increasing attention, both in academia (e.g. colloidosomes) and industry (drug delivery, chemical sensors...). Predicting the dynamics of these objects requires the determination of their mutual interactions. In this work, we focus on the electrostatic interactions between hollow spheres porous to small ions.

We first show that the pair potential between hollow spheres follows the Yukawa form, but with an effective charge for which we provide an analytical expression depending on the solid and solvent dielectric permittivities. This expression is validated numerically by solving the Poisson-Boltzmann (PB) equation around two isolated colloids. The importance of the self-induced electrostatic potential inside the hollow spheres is highlighted.

With the pair potential at hand, we evaluate the performances of two classical approaches providing rapid and easy access to the osmotic pressure of the suspension: the integral equations theory and the cell model. The latter is known to perform well in the solid-like or "electrostatically concentrated" regime, while the former is more accurate for dilute suspensions. Equations of state computed with these models are compared to (i) one-component MD simulations based on the pair potential, and (ii) Brownian dynamics simulations coupled to the full resolution of the many-body PB equation in order to evaluate the different contributions to the pressure (ion entropy, electric field, etc) and to detect possible non-additive effects. The knowledge of this equation of state is of primary importance to determine the gradient diffusion coefficient of the colloids, the latter being required to predict concentration fields in out-of-equilibrium processes like centrifugation, drying, or filtration.



Internal Complexation within Copolymers: An Experimental and Monte Carlo Study on the Effect of Architecture and Interface

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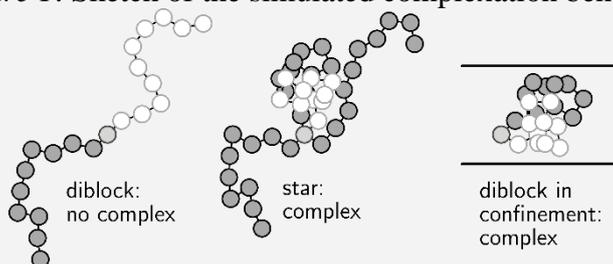
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Experimentally it was found that the local mutual segment density has an effect on the intramolecular complexing behavior of poly(propylene oxide) (PPO) and poly(dimethylaminoethyl methacrylate) (PDMAEMA).^[1] We investigated linear block-copolymers 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.

To further investigate these effects, the polymers were modeled using a coarse grained bead spring model for the polymers. The polymers were made of two types of hard-sphere beads, which interact by an attractive Lennard-Jones Potential.^[2] Using Monte Carlo Simulations the structure of the polymer was observed for different architectures as a function of the attractive strength ranging between $\varepsilon = 0$ and $1 k_B T$. In accordance with the experimental results, the star architecture enhances the complex formation (Figure 1).

Experimental results show a complex promoting effect at interfaces. This is probably due to the increased inherent proximity of the attractive parts of the polymer.^[3] In our simulations the close proximity is created by introducing a spatial confinement. Again, different architectures are compared for a range of different confinements. It was found that the complexation can be promoted by a pseudo-2D environment.

Figure 1: Sketch of the simulated complexation behavior.



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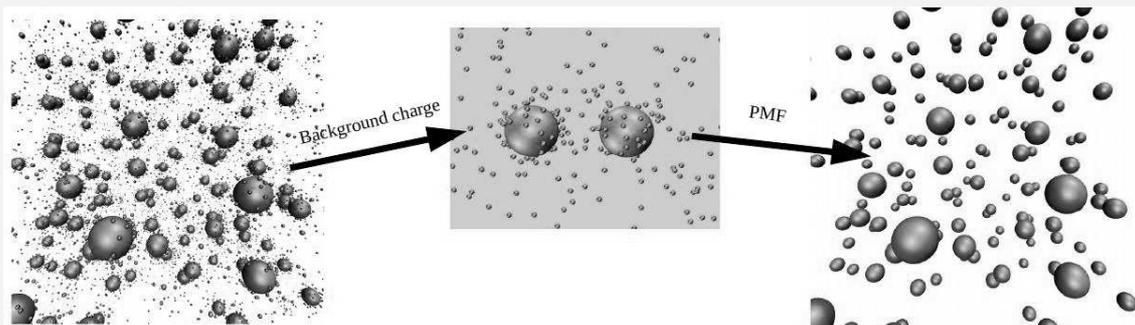
Coarse-graining intercolloidal interactions at high volume fraction

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Simulations of Colloidal dispersion present technical issues due to the great number of degrees of freedom and of space and time scales. One possible workaround consists in determining the effective pair potential between colloids where every solvent or ion degrees of freedom are averaged out. Still, its determination remains tricky in charged colloidal systems because it depends on particle volume fraction, ϕ . Recently, our group [1] developed a simple simulation method to evaluate these effective potentials not limited to weakly coupled system and to isotropic particles. This method consists in calculating the potential of mean force between two colloids placed in a closed cylindrical cell which volume is set to the desired ϕ . It turned out to give excellent results, but is limited to relatively low ϕ as a result of the hard cell boundaries ($\sim 7\%$ for spheres and lower for anisotropic particles [2]). In this work, we propose and test an alternative approach that does not suffer from this limitation. The two colloids are placed instead in a periodic box containing an excess of counterions, neutralized by a uniform background charge, whose concentration is tuned to the desired ϕ . We found a good agreement with the primitive model at volume fractions up to $\sim 30\%$ in both the low and high coupling limit.



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Phase change in aggregate structures of ferromagnetic spherocylinder particles in a suspension by means of Monte Carlo simulations

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Magneto-rheological properties of a magnetic particle suspension are strongly dependent on the formation of aggregates of magnetic particles. This aggregate formation is governed by a variety of factors such as magnetic particle-particle and particle-field interactions, a volumetric fraction and a flow field. A suspension of ferromagnetic rod-like particles can be expected to exhibit strong magneto-rheological characteristics, which is a significantly important factor for application of magnetic particle suspensions to mechanical dampers and actuators. Hence, in the present study, we address a suspension composed of ferromagnetic rod-like particles in thermodynamic equilibrium. We here investigate the dependence of the phase change in aggregate structures on the magnetic field strength for various cases of the magnetic particle-particle interaction strength and the volumetric fraction of magnetic particles. Monte Carlo simulations have been carried out to obtain results of snapshots, orientational correlation function, radial distribution function, order parameters of the system, and so forth. From the present results, it is seen that the cluster formation of magnetic particles significantly appears for a strong magnetic interaction larger than a certain value. In the situation of a weak magnetic field, these clusters do not incline in a specified direction. As the applied magnetic field strength is increased, they come to dissociate into small clusters, and finally at a certain strong applied magnetic field, all clusters completely dissociate into single-moving particles, which all incline almost in the magnetic field direction. This characteristic is in significantly contrast to that of magnetic spherical particle suspensions where stable linear long clusters are formed in the field direction. This clearly exhibits that an applied magnetic field induces the phase change in a magnetic rod-like particle suspension.

Collagen – a new old amphiphile

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Collagen is the most abundant protein in vertebrates, constituting about 30% of all proteins in the tissues of a human body. It can be found in skin, tendons, cartilages, bones, teeth and even blood vessel walls. Collagen molecule is rich in proline and hydroxyproline and consists of three left-handed helical polypeptide chains, rolled into a right-handed triple helix. The helices are cross-linked by a network of intermolecular bonds and intramolecular bridges. Collagen may undergo a number of complex transformations: fibril formation, gelation, gelatinization, denaturation and hydrolysis. The most characteristic for this group of proteins is aggregation into filamentous form – collagen fibrils, which will eventually further aggregate to form collagen fibers, the basic component of connecting tissues. At high temperatures and alkaline or acidic pH, collagen fibrils unfold and dissociate to form gelatin, widely applied in food, cosmetics and photographic industries.

In this contribution we will describe the effect of temperature, partial hydrolysis as well as of the presence of synthetic surfactants on surface activity and surface dilational rheology of collagen (type I from bovine calf skin). The dynamic surface tension was measured during one hour by a drop shape analysis method. The drop volume oscillations were consecutively performed in order to retrieve the surface dilational elastic (storage) and viscous (loss) moduli of the collagen films at the water/air interface. The results show that collagen has a great and underestimated potential as a low-cost biocompatible surfactant.

Polymer crosslinking in the external phase of oil-in-water highly concentrated emulsions

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Highly Concentrated Emulsions, also denoted as High Internal Phase Emulsions (HIPEs), have been used as templates for the preparation of low-density highly porous chitosan foams [1,2]. These materials have been obtained by crosslinking chitosan in the external phase of O/W HIPEs. Genipin, which is a natural reagent extracted from gardenia fruits, was used as crosslinker agent [3]. In the present work, the crosslinking process in the external phase of HIPEs, stabilized with a nonionic surfactant is described. Emulsion stability and rheological properties were studied, in both presence and absence of chitosan. The stability was assessed by measuring droplet size as a function of time, and also by dynamic rheology, where the storage modulus and the cohesive energy density were measured as a function of time [4]. Moreover, emulsions were prepared at different agitation speeds (from 700 to 1200 rpm), to evaluate its influence on droplet size and rheological properties. The results showed that the addition of chitosan led to a pronounced decrease in emulsion droplet size, despite the fact that chitosan did not influence surface tension. This decrease in droplet size was attributed to stronger disruptive tension during emulsification, induced by higher viscosity. The crosslinking of chitosan with genipin was investigated using oscillatory and creep measurements. Both methods showed completion of crosslinking process after 24 h, observing a large increase in storage modulus, cohesive energy and decrease of compliance. Finally, crosslinked chitosan porous foams were obtained after solvent extraction and drying. These materials were observed by SEM, retaining an uniform porous texture.

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LINEARLY SWELLING NON-NIPAM BASED MICROGELS: STRUCTURAL HETEROGENEITIES AS SEEN BY SANS CONTRAST VARIATIONS

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So-called smart microgels are potential building blocks for a lot of different applications like e.g. photonic materials, carriers for catalysts, smart surface coatings and sensors.[1] These particles exhibit a reversible shrinking transition at the lower critical solution temperature (LCST) of the polymer.

In the first part of this contribution, statistical copolymers of N-n-propylacrylamide (NNPAM) and N-isopropylmethacrylamide (NIPMAM) are presented and the use of copolymerisation to tune the LCST of the microgels is discussed.[2] In its second part, this contribution studies non (N-isopropyl acrylamide)-based core-shell microgels that exhibit a unique 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. Our approach was inspired by the work of the Richtering group [3].

The properties of these novel materials are studied by means of dynamic light scattering (DLS) and small angle neutron scattering (SANS). 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. Hence, the core-shell particles behave piezo-like and might be useful as actuators on the nanometer scale [4].

Aiming at a better understanding of the underlying mechanism of the swelling of such core-shell structure, we prepared particles with deuterated cores and used contrast variation in SANS to reveal additional structural features related to the de-swelling and swelling of these microgels.

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HOW DROPS MOVE ON LUBRICANT INFUSED TEXTURED SURFACES

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Liquid repellent, antibiofouling, pressure-stable and self-repairing surfaces would have enormous impact in industrial and medical applications. Slippery lubricant infused textured surfaces may open up novel possibilities. When a liquid drop is deposited on a slippery surface, the drop is found to slip by tilting the surface a few degrees. With the drop, dirt or also bacteria can be removed [1, 2, 3].

We used Laser Scanning Confocal Microscopy (LSCM) to observe the behavior of drops of different liquids on a lubricant infused textured surface. As textured surface we used micropillar arrays and inverse opals to hold different lubricants.

We investigated the shape of the wetting ridge surrounding a drop, the three phase contact lines, and how a drop advances and recedes on slippery surfaces. Single pinning and depinning events are resolved with micrometer and millisecond resolution. Even, cloaking of the drop is visible by using LSCM. Confocal microscopy revealed that drops on slippery surfaces have a high contact angle, typically exceeding 150°.

We expect that this understanding of the stationary and dynamic behavior of drop on slippery lubricant infused surfaces will help to design stable slippery lubricant infused surfaces.

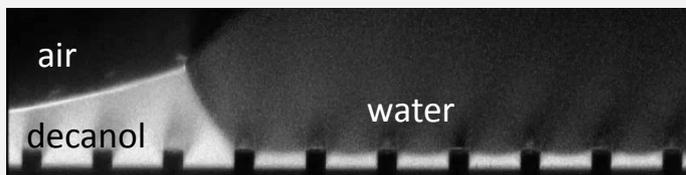


Figure 1: Confocal x-z-image of a water drop stays on a lubricant (decanol) infused pillar surface.

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Sharp Peaks in Viscosity of Mixed Surfactant Solutions Due to “Resonance” Micelle Growth: Experiment and Interpretation

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A sharp peak in the viscosity of surfactant solutions has been experimentally detected at a certain concentration of fatty acid added to the mixture of a zwitterionic surfactant (CAPB, cocamidopropyl betaine) and an anionic surfactant (SLES, sodium laurylesulfate). The viscosity at the peak can reach several thousand times the viscosity of water (Fig. 1 – left) even at a relatively low total surfactant concentration. The highest peak was measured with octanoic acid (HC8). The height of the peak decreases as the chainlength of the added fatty acid increases up to the complete disappearance of the peak for hexadecanoic acid. The cryo-TEM imaging revealed that giant interweaved wormlike micelles form in the vicinity of the peak in viscosity for octanoic acid (Fig. 1 – right). In the case of dodecanoic acid, a transition from cylindrical to disclike micelles has been observed to the right of the peak in line with theoretical predictions [1]. Here, we have further extended the theoretical model, which now accounts for the fact that the replacement of long-chain surfactant molecules with fatty-acid molecules of shorter chains causes a minimum in the micelle free energy vs. fatty-acid concentration. The latter results in a maximum in the mean aggregation number of the cylindrical (wormlike) micelles, thus giving rise to the observed high peaks in viscosity at specific fatty acid concentrations.

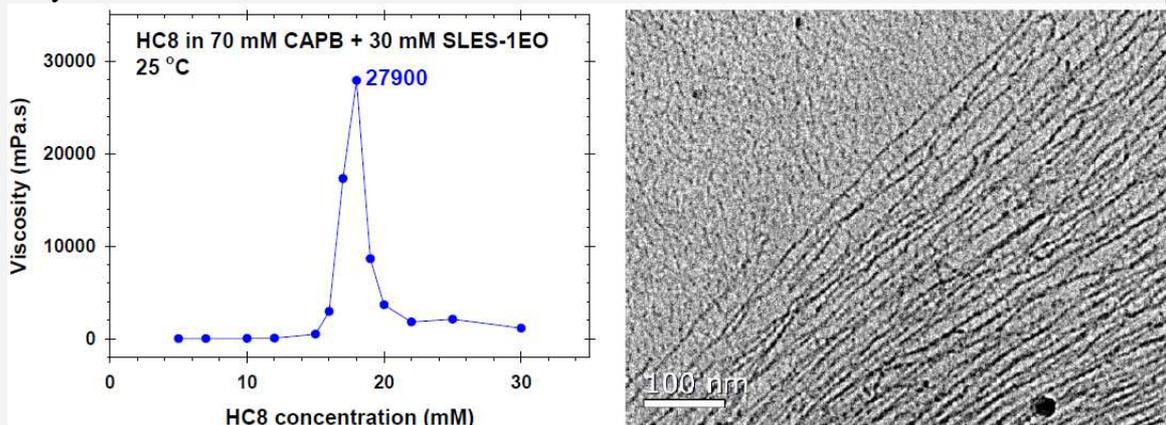


Fig. 1. Viscosity vs. octanoic acid concentration (left) and a cryo-TEM image (right).

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COST CM1101, WG5

Novel emulsion formulation of electrostrictive material for energy harvesting devices

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Micro-sensors and actuators have been used for daily life applications. However the main drawback is their long term autonomy. To overcome to this problem, a promising route is to transform mechanical energy from ambient vibrations to fulfil energy demands of micro-electromechanicals systems (MEMS). A recent approach is the use of polymers loaded with conductive nanoparticles. Near percolated networks of conductive particles yields with giant dielectric permittivity [1] and electrostriction coefficients. Nevertheless, the development of electrostrictive nanocomposites remains challenging. The morphology of the inner network formed by the particles within an elastic polymer has to be finely controlled.

The aim of the present work is the development of near percolated carbon nanotubes (CNT) networks within an elastic polymer matrix, such as polydimethylsiloxane (PDMS). A novel emulsion formulation route is employed to achieve a fine control over the structure of the materials. The nanotubes are dispersed in the continuous phase of an emulsion made of PDMS droplets in water. After water removal, these CNT are segregated, in between the PDMS droplets and can form near percolated networks of morphology controlled by the size of the emulsion droplets. The dielectrics properties of such materials are driven by (i) the droplets size, (ii) CNT concentration and (iii) aggregation state (Fig 1). The improvement of such factors by the emulsion approach leads to giant dielectric constant. A particular attention is now paid to the variations of the dielectric properties in response to a mechanical stress in order to assess the potential of these new materials for energy harvesting applications.

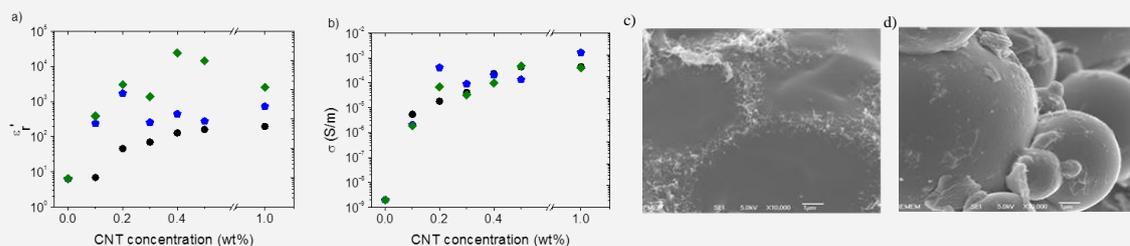


Fig. 1: Dielectric permittivity a) and electrical conductivity b) for three different droplet sizes: 85 μm (dot), 25 μm (pentagon) and 3 μm (diamond). Assessment of the inner cnt network following rapid evaporation c) and slow evaporation d).

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Role of dilute oil-in-water emulsions in the destabilization mechanisms of liquid sheet

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Agricultural spraying involves atomizing a liquid stream through a hydraulic nozzle forming a liquid sheet, which is subsequently destabilized into drops. Standard solution adjuvants as dilute oil-in-water emulsions are known to influence the spray drop size distribution. We will present model laboratory experiments that aim to elucidate the physical mechanisms causing the changes of drop size distribution.

Model laboratory experiments based on the collision of a liquid drop on a small solid target are used to produce and visualize liquid sheets [1]. With dilute oil-in-water emulsions, the liquid sheet is destabilized by the nucleation and growth of holes within the sheet that perforate it during its expansion. The physical-chemical parameters of the emulsion, such as the emulsion concentration, the chemical nature of the components and the emulsion drop size distribution, are varied to rationalize their influence on the perforation mechanisms.

Thanks to an original technique that we recently developed to access the time and space-resolved thickness of the sheet [2], we measure that the formation of a hole within the sheet is preceded by a localized thinning of the liquid film. We show that this thinning results from the entry and spreading of emulsion oil droplets at the air/water interface. The oil droplet spreading, due to Marangoni driven surface tension gradient, drags subsurface fluid with it. This subsurface flow causes a local film thinning which can ultimately rupture the film. Quantitative analysis of the spreading dynamics unambiguous confirms the physical mechanism at the origin of our observations.

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Microcapsules Based on Pickering Emulsion

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Microencapsulation is used to produce cosmetics, paints and pesticides useful for our daily life. The diversity of applications and the variety of encapsulated products offer large industrial prospects. Thus, encapsulation is an extremely dynamic area of research, showing multidisciplinary and tremendous competition. Capsules become always more sophisticated and specific.

We propose a new synthesis path that combines emulsions science and sol-gel chemistry, where Pickering emulsions and the associated limited coalescence allow generation of monodisperse drops. Functionalized silica particles irreversibly adsorbed at the oil / water interface confer high stability to emulsion. In a second step, to obtain capsules, a shell is synthesized around the droplets. Indeed, the sol-gel method allows the formation of a rigid and brittle shell at the oil/water interface by hydrolysis and condensation of a silica precursor, the tetraethyl-orthosilane (TEOS). The adsorbed particles favor nucleation events for the mineralization step conferring the shell.

This process gives reproducible results with drop sizes of about 7 microns and a 50 nm shell thickness (Figure 1.). By varying the amount of silica particle and the amount of TEOS, it is possible to obtain a range of capsules by tuning the drop size and the shell thickness. This type of approach offers an interesting route to produce capsules for which the release can be provoked by a mechanical threshold pressure.

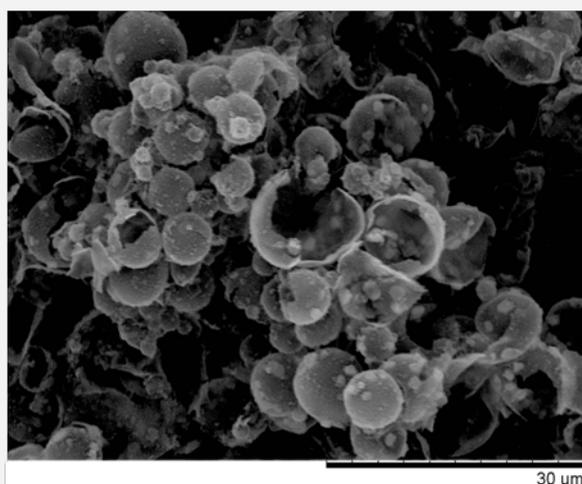


Figure1. Image by scanning electron microscope of mineralized capsules from a direct emulsion of 7 μm .

Interfacial properties of binary mixtures of partially fluorinated alkanes and DPPC: A PM-IRRAS study

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The interfacial behavior of partially fluorinated alkanes [$C_nF_{2n+1}C_mH_{2m+1}$ or (F_nH_m)] and the gemini-type alkanes [$(C_nF_{2n+1}CH_2)(C_{m-2}H_{2m-3})CH-CH(C_nF_{2n+1}CH_2)(C_{m-2}H_{2m-3})$ or di(F_nH_m)] has been investigated employing the monolayer technique. It is notice that these (including gemini-type) alkanes are possible to form a monolayer at the air-water interface as opposed to the corresponding hydrogenated alkanes. In previous work, it has been implied that $F10Hm$ and di($F10Hm$) tends to form densely packed surface micelles on water, where dipalmitoylphosphatidylcholine (DPPC) molecules which is a major component in pulmonary surfactants are spread at the same time. Surface pressure (π)-molecular area (A) and surface potential (ΔV)- A isotherms indicated the kink points corresponding to the surface micelle formation. Moreover, the formation was supported morphologically with Brewster angle microscopy (BAM), fluorescence microscopy (FM), and atomic force microscopy (AFM). In the present study, we have investigated the surface micelle formation of $F10Hm$ and di($F10Hm$) in the DPPC monolayer from the spectroscopic aspect employing in situ polarization modulation-infrared reflection adsorption spectroscopy (PM-IRRAS).

Observation of Rose Petal Effect on Single Scale Roughness Surfaces

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In 2008, Jiang and coworkers [1] pointed out that the rose petals possess the characteristic of super-hydrophobicity with strong adhesion to pin water drops. This phenomenon is well known as “petal effect”. It is generally believed that the petal effect is attributed to dual scale roughness and the water droplet can penetrate into the micro-scale roughness but not the nano-scale roughness. In this study, a surface of the single scale (either micro-scale or nano-scale) roughness within certain roughness region is observed to exhibit petal effect. A series of micro- and nano-pillar-like patterned surfaces with different roughnesses are fabricated. The advancing/receding contact angles and sliding angle of a water droplet on these patterned surfaces are carefully measured. When the surface roughness is increased and carefully tuned, a patterned surface of petal effect is consistently observed. That is, the dual-scale roughness is not a necessary condition for a surface of petal effect. [2] Simulation results of the metastable states of a liquid droplet deposited on a hydrophobic sinusoidal surface by using the Surface Evolver [3] are discussed and applied to support the viewpoint that single scale roughness surface could exhibit the petal effect.

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Electroconductive oil formulation by tubular network of molecular self-assembly

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Electroconductive organic soft matters have potential applications for solar cells, batteries, lubricant oil for precise machines, etc. In this presentation we propose a novel approach to formulate electroconductive oil by network formation of surfactant molecular self-assembled structure. We employed two surfactants, sorbitan laurate (Span20) and poly(oxyethylene) sorbitan monooleate (Tween80) for tubular network formation in oil. Electrorite (KCl) and ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [C₄mim][BF₄]) aqueous solutions were added to the network structure for electroconductive path.

Fig.1 shows electroconductivity change with temperature in the KCl (or [C₄mim][BF₄]) aq./Span20/Tween80/isopropyl myristate (IPM) system with oil/surfactant=8/2 and Span20/Tween80=3/2. In the KCl aq. system, electroconductivity was almost constant below 18°C and increased above 18°C, then, it decreased above 32°C. The maximum electroconductivity was approx. 0.8 μS/cm. In the [C₄mim][BF₄] system, electroconductivity also reached to the maximum at 32°C but the maximum conductivity was approx. 10 μS/cm which is more than 10 times higher than the KCl system.

Network structure was characterized by small angle X-ray scattering (SAXS). SAXS spectra were analyzed by the generalized indirect Fourier transformation (GIFT) method to obtain pair distance distribution function (PDDF). PDDFs showed tubular structure at all temperatures measured in the [C₄mim][BF₄] system. Tubes grew up to 35°C and was changed to the opposite direction above 35°C. This suggests that the electroconductivity behavior was changed by the growth of tubular network.

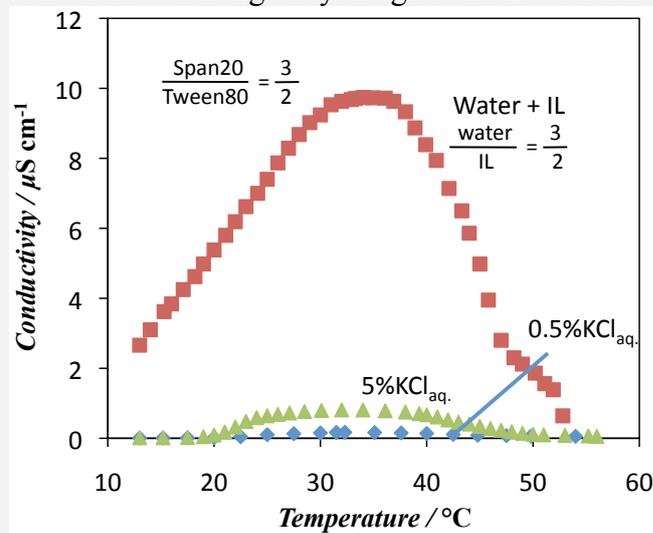


Fig.1 Electroconductivity change against temperature

Coupled Nanotubular J-Aggregates and Quantum Dots for Efficient Resonance Excitation Energy Transfer

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Resonant coupling between distinct excitons in organic supramolecular assemblies and inorganic semiconductors is supposed to offer a new approach to design novel optoelectronic devices. Here, we report on colloidal nanohybrids, which consist of supramolecular tubular J-aggregates decorated with semiconducting quantum dots (QDs) via an electrostatic self-assembly process [1]. The role of the QD in the energy transfer process can be switched from donor to acceptor by tuning its size and thereby the band gap while keeping the chemistry unaltered. The tubular structure of the J-aggregates remains unaltered and the particles are located within a close distance to the aggregate surface of less than 4 nm. The close proximity of J-aggregates and QDs results in strong excitation energy transfer coupling, which is close to 100% for the case of energy transfer from the QD donor to the J-aggregate acceptor and approx. 20% for the reverse case. This system demonstrates a model for an organic-inorganic light harvesting complex using methods of self-assembly in aqueous solution and highlights a possible route towards hierarchical synthesis of structurally well-defined supramolecular objects for advanced functionality.

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Pattern Deposition in the Presence of Surface Acoustic Waves (SAWs)

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Abstract

The use of functional surfaces in the areas of electronics, semiconductors, photonics, biotechnology, etc., is long-established. Conventional techniques used for making such functional surfaces are photolithography, ink-jet printing, spin-coating. In the present study we use the natural self organisation of colloidal particles, following the dewetting of a carrier liquid upon its evaporation, in addition to active SAW interference with this process in order to produce two dimensional structures and patterns. An interplay between the flow field within an evaporating suspension of colloidal particles and the dewetting motion of the suspension three phase contact line governs the deposition kinetics of colloidal particles in geometrical patterns on the solid substrate. Consequently this interplay determines the geometry of these patterns. In the present study we use surface acoustic waves (SAW) to manipulate the motion of the three-phase contact line and thus the deposited patterns. The SAW generates stress in the vicinity of the contact line between the liquid and the solid and thus intervenes with the dynamics of the receding front of the liquid that undergoes dewetting due to evaporation. Consequently the SAW may interfere with the deposition of patterns. We show that using SAWs we are capable of actively altering the dynamic state of the deposition, changing the qualitative geometry of the deposited patterns, and further alter the location of patterns on the solid substrate.

Interactions of lanthanide cations with phospholipid micelles

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Separation of lanthanide cations using liquid-liquid extraction has become a center of focus for the nuclear industry in the context of nuclear waste recovery, but also given the self-value of lanthanides and the fact that their worldwide resources are limited. The interaction of lanthanides with extractants always has a strong complexation component, but there are several issues involved that are clearly related to interfacial science. In this work we examine in detail the interaction of a series of lanthanide cations with micelles of the single-chain phospholipid dodecyl phosphocholine (DPC) in aqueous solutions (used as a prototype extractant), by means of fluorescence spectroscopy, isothermal titration calorimetry, SAXS and rheology. The interaction is quite strong, and surprisingly it depends on the – supposedly neutral – anion of the lanthanide salt. In many cases the interaction leads to precipitation of the lipid or even gelation, while the presence of additional simple electrolytes can have profound effects. Both anionic and cationic effects on the lanthanide- DPC complexation have been detected. The results highlight the complexity of the interactions in extraction systems and the need for detailed physicochemical and interfacial studies, in order to better design these important processes.

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Contribution from COST CM-1101 network, Working groups 2 and 5

Protein-drug molecule interactions characterized by thermodynamic state functions using 2D and 3D experiments

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Protein-biomolecule/drug molecule interactions play an important role in the health care. Detailed quantitative, kinetic and thermodynamic characterization of these biomolecular interactions may decisively contribute to the modern pharmaceutical developments. Numerous different analysis are available that can be used to monitor and quantify these bindings. However the radio-labelled assays are fast and reproducible techniques, their major disadvantages are that they are hazardous to human health. This has led to the development of “label-free” assays based on optical methods. The two-dimensional (2D) sensor techniques especially the SPR, are capable of real-time monitoring of these interactions without the use of labels. Major limitation is only that one of the binding partners needs to be immobilized on a sensor chip surface. However, the SPR is a well-known technique to investigate biomolecular interactions, but only a few articles give information about the temperature-dependency of the biomolecular interactions. Investigation of temperature-dependent adsorption phenomena at solid/liquid interface permits the determination of thermodynamic state functions (ΔG , ΔH , ΔS) of the interaction. The van't Hoff analysis has been used for thermodynamic studies. More recently, the use of sensitive microcalorimetric techniques (ITC) in solutions (in 3D systems) in controlled drug release research is emerging.

In our work various protein-drug molecule interactions have been studied by SPR adsorption experiments. Important quantitative, kinetic and thermodynamic data have been determined. For comparison the thermodynamic state functions in solutions have been determined by ITC studies as well.

Charge-Induced Patchy Attractions Between Proteins

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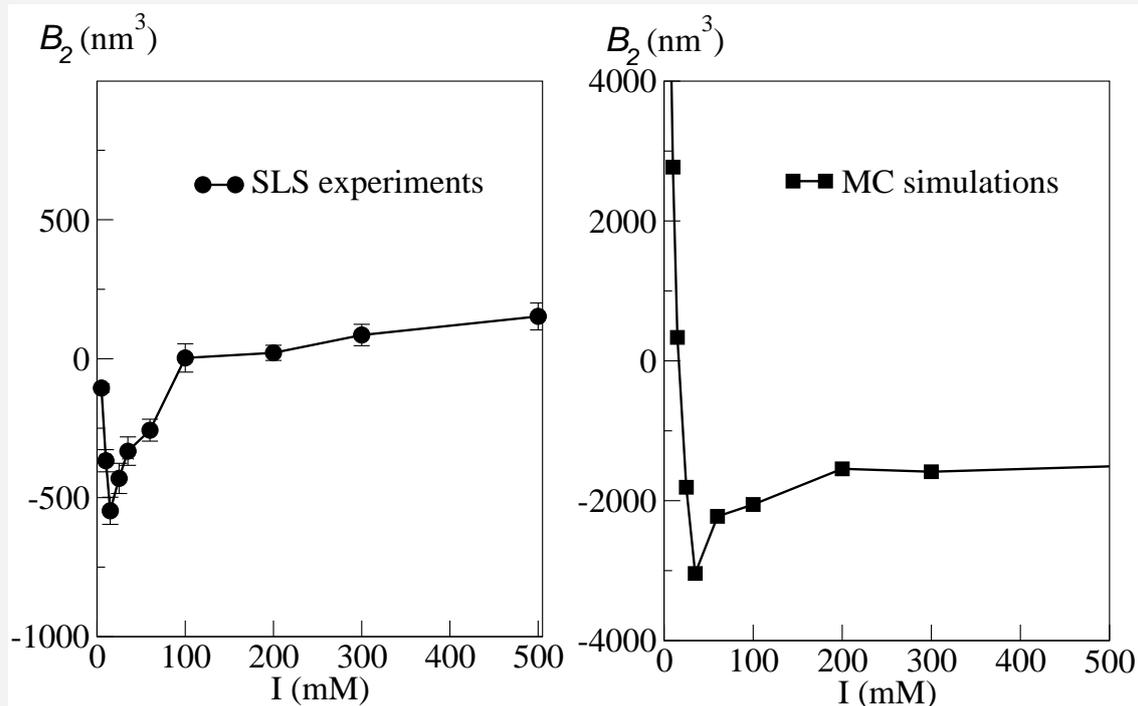
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We report static light scattering (SLS), small-angle X-ray scattering (SAXS) and structure-based Monte Carlo (MC) simulations providing new insights into the mechanism of anisotropic attractions between globular proteins. The presence of an electrostatic patch, localized and highly directional, gives rise to measurable attractions. The attractive patch, together with Coulombic repulsion, result in two counteracting electrostatic contributions to the interaction potential. Overall, this is manifested in a non-monotonic behaviour of the second virial coefficient, as a function of ionic strength [1]. The model for protein interactions used in the MC simulations is in good agreement with the SLS experiments. From analysis of structure factors, obtained from both SAXS and SLS, signs of anisotropy will be discussed.



I am applying for the Enzo Ferroni award.

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Smart hybrids: Functional gold nanoparticles incorporated into stimuli-sensitive polymer brushes

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Work group 4

The modification of surfaces by coating with polymer brushes has attracted much interest in the past few years due to numerous potential applications in material and life science for the development of smart surfaces. They can be used as 3D matrices for the immobilization of nanoparticles, resulting in nanocomposite materials with interesting mechanical, optical, or catalytic properties with tailored functions [1]. Using stimuli sensitive polymers allows controlling the distribution of the particles during and after particle loading, which is of high impact for sensor applications.

Knowledge about the (spatial) structure of brush/particle hybrids is rather restricted. In order to enhance the functionalities of brush/AuNP-based optical sensors, it is of crucial interest to understand the forces acting between polymer and particles. Studying the mutual influence of the brush matrix and the attached AuNPs on the structure of the resulting brush/AuNP hybrid will allow fine-tuning of the particle loading and distribution.

In this study, responsive poly-(*N,N*-dimethylamino)ethyl methacrylate (PDMAEMA) and poly-(*N*-isopropylacrylamide) (PNIPAM) brushes are used as a matrix for the attachment of gold nanoparticles (AuNPs). We find that the uptake and distribution of nanoparticles in polymer brush matrices is highly dependent on the brush thickness [2], brush grafting density [3], polymer chemistry, particle surface functionalization and particle size. The stabilizer (insulin or citrate) of the AuNP affects the distribution within the brush.

These smart hybrids can be used as colorimetric sensors and present a model system for protein adhesion/embedding.

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Balancing surface physical activity and bioactivity of short peptide amphiphiles

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Small peptide amphiphiles are usually comprised of a hydrophobic tail containing several hydrophobic amino acids and a hydrophilic head containing fewer hydrophilic (polar or charged) amino acids. Unlike conventional surfactants, peptide amphiphiles readily adopt secondary structures such as alpha-helices and beta-sheets. Thus, their structures often mimic some native protein sequences and may not display any obvious amphiphilic characters. Over the past 10 years or so, we have studied 2 groups of small peptide amphiphiles, with the first group bearing structural similarity to conventional surfactants and forming beta sheets and the second group bearing a classical protein helical sequence hallmark and forming alpha helices under membrane mimic environment. In this talk, we will show the surface adsorption and membrane penetration behaviour of these short peptides from different model lipid membrane systems. We will then show how changes in the molecular structures of these peptides can enhance their potency in killing bacteria and inhibiting cancer cell growth whilst showing reduced toxicity to mammalian cell hosts in co-culturing. We have been trying to provide a mechanistic insight of the selective responses to different cell types by forming different lipid models from which cell selectivity and toxicity can be replicated via different molecular interactions. We demonstrate how Langmuir film experiments, biosensor studies and neutron reflection and scattering offer valuable information about how peptides interact with different membrane systems mimicking different cell types, thereby providing mechanistic insight at the molecular level.

Kinetics and dilational rheology of β -lactoglobulin adsorption at the water/oil system at different pH and ionic strength

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Proteins, in general, adsorb at liquid interfaces and are well-known as efficient stabilizers of foams and emulsions [1, 2]. β -lactoglobulin (BLG) is one of the most widely studied ones due to its major industrial applications particularly in food processing.

Oscillating drop tensiometry was applied to study adsorbed protein interfacial layers at water/oil interfaces [3]. In this work, the influence of different pH and ionic strength on the dynamics of BLG water/tetradecane interface has been investigated. Dynamic interfacial tension (γ) and interfacial dilational elastic modulus (E') of BLG solutions at three different pH values of 3, 5 and 7 and at three different ionic strength are measured by Profile Analysis Tensiometer (PAT-1, SINTERFACE Technologies, Berlin). Furthermore, interfacial tension and dilational rheology of mixed solutions of BLG and with the anionic surfactant SDS (sodium dodecyl sulphate) of varying protein/surfactant concentrations have been also studied.

The presented results of the adsorption isotherm and the dilational visco-elasticity under equilibrium and dynamic conditions is based on measurements of the dynamic interfacial pressure and its response to sinusoidal drop area variations.

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Multilayers of Lung Surfactant at the Air-Water Interface Observed by Neutron Reflectometry under Compression-Expansion Cycles

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We have used neutron reflectometry to study lung surfactants at the air-water interface under controlled high humidity and repeating compression-expansion cycles to mimic the work of breathing. We used Curosurf, a porcine extract currently used in clinical application to treat infants suffering from neonatal respiratory distress syndrome (NRDS). We spread the lung surfactant extract (Curosurf) on an aqueous subphase and show how the multilayers develop at the interface during the compression expansion cycle of surface film. Multilayers have been observed in solutions of similar extracts before but in static experiments as a function of time [1]. Here we spread the aqueous lung surfactant dispersion (Curosurf) at the interface by using a glassrod according to the method of Trurnit [2]. We demonstrated that the formation and properties of the multilayers at the air-water interface are responsive to compression-expansion cycle of surface film as well as to subphase ion composition and temperature.

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Competitive adsorption between bulk food proteins and hydrophobin HFBII related to foam stability

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Over the last few years, the class II hydrophobin HFBII has gained increasing interest in both academia and industry for several applications such as surface modifications or for emulsifying or foaming properties. For example, HFBII can provide extreme stability against bubble dissolution and foam coarsening. The underlying mechanisms have been increasingly understood.

When it comes to application of HFBII in complex formulations, this molecule will inevitably co-exist with other surface active molecules such as proteins, in some cases at elevated levels, where it is known that strong competition at the air-water interface can be expected. This could eventually lead to loss of functionality of HFBII as foam stabiliser.

In this presentation, we will present a novel approach to control this competition by bulk proteins and discuss a systematic experimental approach on how to characterise the surface properties of the bulk protein solutions. These properties will then be related to foam stability data.

Influence of the cross-linking density of PNiPAM microgels on the drainage dynamics of thin-liquid films

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Pickering emulsions stabilised with microgels formed from the thermosensitive polymer PNiPAM are both very stable and able to be destabilised on demand. The stability of microgel emulsions is linked to the properties of the thin films separating neighbouring droplets, but the dynamics within these films are not well understood. In order to study adsorption and drainage dynamics of these films a single thin film in air was examined with white light interferometry.

Using a hydrostatic thin film balance setup the time evolution of the film thickness was studied for a set applied pressure. Softer microgels, those with a lower cross-linking density, have been shown to stabilise better than harder microgels, so two cross-linking densities of microgels were examined to explore the origin of this difference. Concentration was varied to control surface coverage. The influence of time allowed for adsorption before pressure drop was also explored.

Results recover the increased stability of films formed from soft microgels, and of those with higher surface coverage. Mechanical stability of emulsions is reduced by adhesion between film surfaces.

Films formed from lower concentrations or with harder microgels were more likely to exhibit sudden nucleation to adhesive bilayer or monolayer under pressure, accompanied by a large increase in plateau border contact angle. Film reswelling experiments confirmed adhesion for nucleated layers.

Buckling of paramagnetic chains in soft gels

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We study the magneto-elastic coupling behavior of paramagnetic chains in soft polymer gels exposed to external magnetic fields. To this end, a laser scanning confocal microscope is used to observe the morphology of the paramagnetic chains together with the deformation field of the surrounding gel network. The paramagnetic chains in soft polymer gels show rich morphological shape changes under oblique magnetic fields, in particular a pronounced buckling deformation [1]. The details of the resulting morphological shapes depend on the length of the chain, the strength of the external magnetic field, and the modulus of the gel. Based on the observation that the magnetic chains are strongly coupled to the surrounding polymer network, a simplified model is developed to describe their buckling behavior.

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Droplet fragmentation in microfluidic devices

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We study both experimentally and theoretically the fragmentation of droplets colliding with a microfluidic obstacle placed in a conduct, a phenomenon which occurs when the capillary number at play exceeds a critical value. When the distance between droplets is large enough so that they are isolated hydrodynamically, we identify the seven dimensionless parameters of the problem that control fragmentation. We introduce a simple theoretical framework that allows one to well predict the no-breakup/breakup transition and the volumes of the two daughter droplets produced when breakup occurs in terms of all possible experimental variables [1,2]. Our findings outline the crucial role played by the viscosity contrast between disperse and continuous phases on the breakup of confined objects. By working with one-dimensional periodical assemblies of drops, we also show the possible emergence of complex fragmentation dynamics for which the sizes of the daughter droplets created upon breaking of mother drops may become a periodic function of time. We demonstrate that this phenomenon results from time-delayed feedbacks between successive breakup events induced by drop-to-drop hydrodynamic interactions. We derive the existence of numerous bifurcations between periodic regimes and we establish diagrams mapping the various regimes observed as a function of the governing (physicochemical, hydrodynamic and geometrical) parameters.

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Micro-structuration of polymer and metal surfaces using colloids and electric fields; electro-colloidal lithography

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Surface patterning usually requires sophisticated, time consuming and expensive techniques. Colloidal lithography has been developed for the last thirty years to propose an alternative to these intricate techniques. However, colloidal lithography usually requires additional “classical” techniques which make this process not so advantageous. We recently developed a new patterning process, called electro-colloidal lithography (ECL) which is easy to handle, cheap and rapid. It consists in using oscillating (AC) electric field to assemble colloidal particles, and to use a continuous electric field to deposit either their content (after electrochemical reduction), or another population of colloidal particles.⁽¹⁾

In that presentation, we will detail the principle of ECL and will illustrate its potentialities giving examples of patterned surfaces: polymer^(1,2) and metal ones⁽¹⁾ (Fig. 1). We will notably demonstrate for the first time the ability of liquid colloidal particles (double emulsion globules) to self-assemble into 2D crystals under AC field,⁽³⁾ exactly like solid particles (Fig.2).

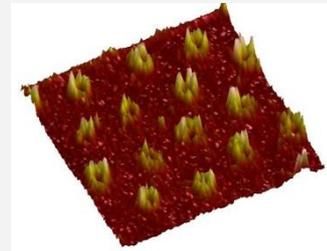
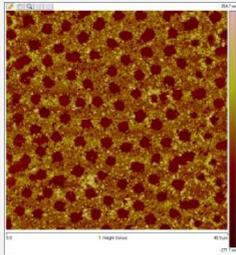


Figure 1 : Patterned polymer surface (left) and metal patterned surface (right) produced by ECL

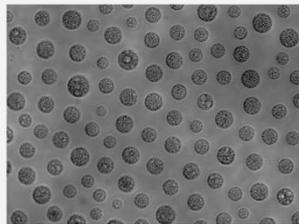


Figure2: Double-emulsion globules organized under AC field

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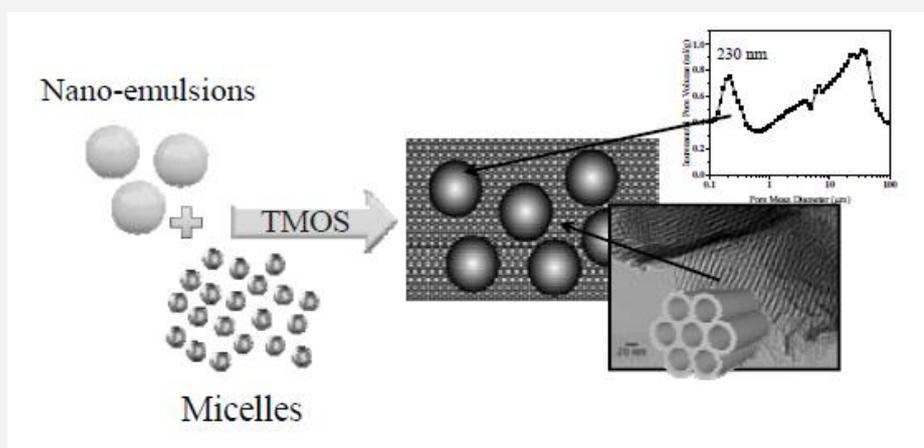
Detailed Investigation of Nano-Emulsions Obtained from the Remcopal 4 / decane / Water System and Their Mineralization

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Dual templating is a technique used to design porous material with two pore sizes ranging from a few nanometers to several micrometers. In the literature the use of nano-emulsion to prepare porous materials is barely reported. But, due to their properties nano-emulsions are excellent candidates to be used as imprints to create a macropore network [1-3]. In this study after the detailed investigation of the Remcopal 4/decane/water system, nano-emulsions have been formulated and characterized to better address their mineralization by a dual templating mechanism together with Pluronic P123 micelles. After removing the organic matter, meso-macrostructured silica materials are obtained. Small angle X-ray scattering patterns of the materials and transmission electronic microscopy experiments show that the mesoporous network (mesopore size around 9 nm) adopts a hexagonal arrangement. Changing the P123 concentration the mesopore size can be tuned from 6.9 to 9.3 nm. The size of the macropores determined by mercury porosimetry is around 230 nm. We have also evidenced the dual role plays by the Pluronic micelles. They not only induce the mesopore network through the cooperative templating mechanism, but their presence also favors the mineralization of the nano-emulsions.



Preparation of macro-mesoporous silica from nano-emulsions

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Porous elastomer systems for acoustic metamaterials

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Metamaterials are artificially structured materials in which the propagation of light, sound or heat waves is nonconventional, which results in anomalous refraction or extremely high attenuation. In the case of sound, the propagation of wave with frequency ω is mediated by the values of the dynamic mass density $\rho(\omega)$ and the elastic modulus $\kappa(\omega)$ of the medium. As first shown by Li and Chan (*Phys.Rev.E* 2004), the functions $\rho(\omega)$ and $\kappa(\omega)$ can be modulated using a system of Mie resonators, i.e. inclusions exhibiting very low sound velocity with respect to the surrounding matrix. At frequencies slightly above the monopolar and dipolar resonances of these “ultra-slow” inclusions, the phase velocity $v(\omega)=(\kappa(\omega)/\rho(\omega))^{1/2}$ can be made negative as well as the acoustic refractive index $n(\omega)=v_0/v(\omega)$, where v_0 is the phase velocity in the surrounding matrix.

Due to the combination of relatively high (compared to gas) mass density with very low elastic modulus, porous materials demonstrate very low sound velocities and appear as the best materials for Mie-type acoustic resonators. Recently, Brunet et al. (*Nature Mater.* 2014) obtained a metamaterial with negative acoustic index in the 150-250 kHz frequency range using porous silicone beads dispersed in an aqueous gel. The sound velocities in such beads have very low values (below 100 m/s) providing excellent contrast with the medium (1500 m/s). However, no direct measurements of mechanical properties of the beads were provided.

Here we show that the elaboration conditions strongly impact the porous structure of the silicone beads and their mechanical and acoustic properties. We use two different inverse water/PDMS emulsions to obtain porous beads and show which type of structure is necessary for obtaining the resonance phenomenon and the negative refractive index.

This work was performed under the auspices of the Labex ANR-10-LABX-0042-AMADEUS with the help of French state Initiative d'Excellence ANR-10-IDEX-003-02.

Characterization and control of Norovirus interactions and their impact on virus stability and infectivity

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We characterize the colloidal interactions of Norovirus virus-like particles (VLPs) in aqueous solution and on surfaces and seek means to control and modify them by using various classes of surfactants. The fundamental understanding of these interactions will aid in practical formulation of novel mixtures for virus inactivation and removal from contaminated surfaces. In aqueous solution, we characterize the effects of solution pH and surfactant type and concentration on virus particle aggregation, dispersion, and disassembly using dynamic light scattering (DLS) and electrophoretic light scattering (ELS). We observe that a strong ionic surfactant above its critical micelle concentration (CMC) causes capsid disassembly and breakdown of aggregates. Below CMC, surfactant adsorption onto the virus capsid follows simple adsorption models, depending on the charge of the surfactant and the net charge of the capsid. Ionic surfactant adsorption leads to modified apparent surface charge and subsequent aggregation or dispersion, depending on the surfactant charge. Our immunoassay for detection of surface-bound VLPs demonstrated that compared to other classes of surfactant, anionic surfactant removes the most VLPs from a hydrophilized glass slide, possibly due to strong steric stabilization. We also characterize the effects that copper ions have on virus colloidal interactions to explain empirical data indicating virus inactivation by copper alloy surfaces and to develop novel metal ion-based virucides. Above the isoelectric point of Norovirus VLPs, very low concentrations of divalent copper ions (~1 μM) rapidly bind and aggregate the particles. Below the isoelectric point of the VLPs, copper ions do not induce VLP aggregation. Copper binding to the capsid surface and subsequent virus aggregation depends on the amino acid composition of the major capsid protein and varies significantly across different Norovirus strains. We seek to use the interaction and infectivity data reported here to design an effective and benign nanoparticle-based delivery system for virucidal copper ions.

Skin penetration of ions

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Though it was early thought that ionic species could not penetrate the skin because they were quite hydrophilic, it is now clearly established that there are several penetration paths for ions through skin. The barrier to skin penetration is the stratum corneum consisting of corneocytes imbedded in a continuous lipid matrix. Therefore ions penetration depends on their hydrophilic/hydrophobic properties described by the Hofmeister series. The purpose of the study was to sort skin penetration of anions with respect to their properties and to assess the paths and the mechanisms of ion penetration.

Penetration of ionic species through skin was first investigated by measurements of their permeation through full thickness excised skin by passive diffusion. The distribution of ions stored in the different skin layers, *stratum corneum*, viable epidermis and dermis was determined. Along the halides series, the most hydrophobic iodide penetrated the most. The order followed the Hofmeister series: $I^- > Br^- > Cl^- > F^-$. The storage of anions in the *stratum corneum* followed the same order.

The penetration of mixed anions was complex since the presence of a hydrophobic anion promoted the penetration of its more hydrophilic partner. It appeared that hydrophobic anions acted as penetration enhancers for hydrophilic anions. Experiments were performed in order to identify the diffusion path, either through corneocytes or through the lipid matrix, involved in such a synergistic effect.

Active penetration by ion channels and ion pumps supplement the passive diffusion. Experiments were designed to discriminate active and passive diffusion, either by comparison of fresh viable skin and non-viable skin after freezing, or by blocking the ion transporters present in the top viable epidermis (*stratum granulosum*) with inhibitors.

Suitable Synthesis Strategies of Nanoporous Melamine-Formaldehyde Particles

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Nanoporous materials derived from organic materials have attracted enormous attention during the last years due to their potential application as separation media and catalyst support.[1-4] Amino resins are highly cross-linked leading to a good stability against harsh pH-values and organic solvents as well as thermal resistance. Furthermore, the high amount of amino functionalities in the polymer network results in promising adsorption properties. We designed and synthesized low-cost, spherical nanoporous amino (melamine, thiourea, urea, and formaldehyde) resin particles based on a hard-templating technique. Melamine-formaldehyde (MF) was synthesized by a) starting with the commercially available oligomer solution and b) starting with the monomers itself keeping all other synthesis conditions constant. The obtained products feature completely different macroscopic appearance. The finer details of the shape control and templating strategies are discussed. Furthermore, the obtained MF particles are compared with other amino resin particles. All particles offer specific surface areas between 250 m²/g and 350 m²/g.

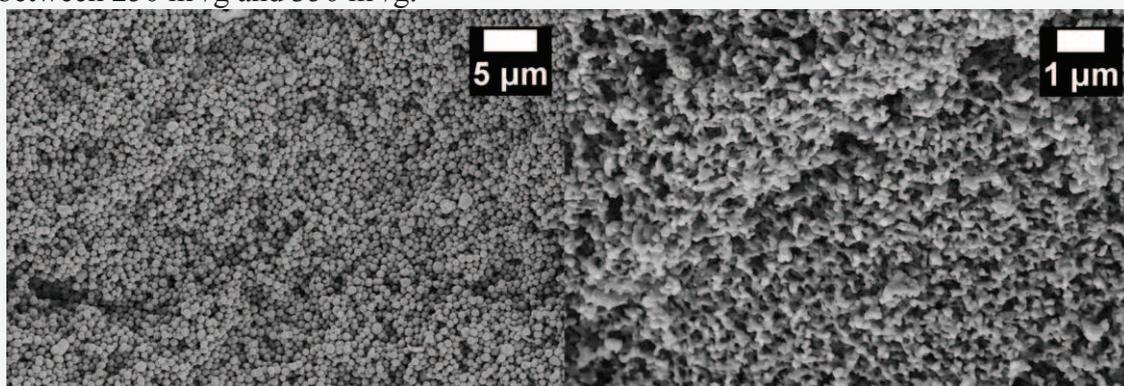


Figure 1. exemplary scanning electron microscopy (SEM) image of melamine-formaldehyde (MF) particles using the monomers as starting material (*left-hand-side*) and exemplary SEM image of MF particle clusters obtained by using an oligomer solution (*right-hand-side*).[3]

Finally, first results of the adsorption properties in terms of heavy metal ions in aqueous solution as well as CO₂ adsorption properties will be discussed. In impact of the pore size and the different chemical moieties, the adsorption properties of the amino resin particles will be analysed and discussed.

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Industrially-relevant polymerization-induced self-assembly formulations in non-polar solvents: RAFT dispersion polymerization of benzyl methacrylate

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Industrially-sourced mineral and poly(α -olefin) (PAO) oils are used as solvents for the reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization of benzyl methacrylate (BzMA) using a poly(lauryl methacrylate) macromolecular chain transfer agent (PLMA macro-CTA) at 90 °C. The insolubility of the growing PBzMA chains under such conditions leads to polymerization-induced self-assembly (PISA).^{1,2} The particular diblock copolymer composition required to access a specific morphology (Figure 1: spheres, worms or vesicles) depends on the nature of the oil. Moreover, the solvent type also affects important properties of the physical free-standing gels that are formed by the PLMA-PBzMA worm dispersions. An efficient ‘one-pot’ protocol for the synthesis of PLMA-PBzMA diblock copolymer spheres at high solids concentration has been developed. This work is particularly relevant in light of the recent report by Zheng et al.,³ where diblock copolymer spheres dispersed in non-polar solvents significantly reduced the friction coefficient of lubricant base oils in the boundary lubrication regime.

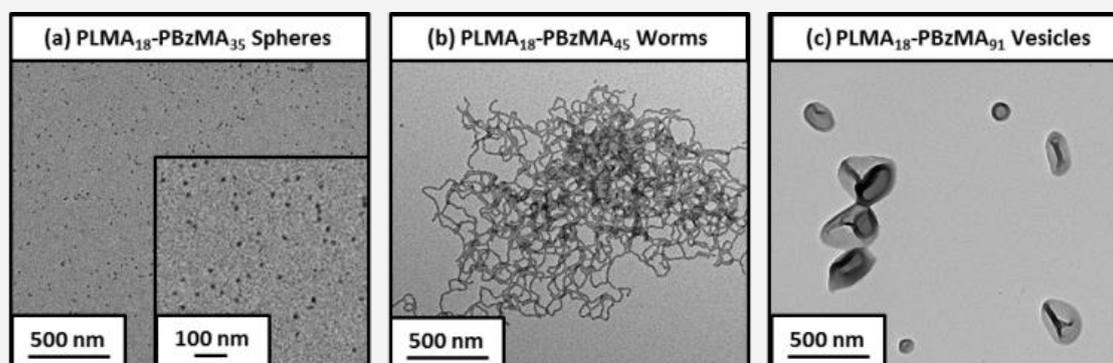


Figure 1. Representative transmission electron microscopy (TEM) images of PLMA-PBzMA spheres (a), worms (b) and vesicles (c).

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Structure and Dynamics of Particles at Fluid Interfaces.

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Particles trapped at fluid interfaces are increasingly used for substituting synthetic surfactants in stabilizing dispersed systems such as emulsions and foams[1]. Furthermore, they can be used as model systems of 2D fluid and solid systems. Even though questions remain open about the interparticle interactions and the particle density dependence of the 2D system, the particle dynamics at the interface, and their use as probes for measuring the shear viscosity of surfactant and polymer monolayers is still rather controversial. The dynamics is very important because it is responsible of the response of emulsion droplets to external mechanical perturbations such as the collisions between droplets. It is also important to the response of the interbubble walls to the shear field due to liquid draining.

In this communication after a brief review of the structure and phase diagram of particles (from 1 to 5 μm) monolayers [2] and the role played by the three-phase contact angle [3], we will examine the dynamics of particles in these quasi-2D systems. In particular, the particle mean square displacement variation on going from dilute (fluid-like) monolayers to concentrated (solid-like) ones will be discussed, and these results compared with the dynamics of particles trapped in an optical tweezers system.

Finally, we will show that following the dynamics of a few particles embedded in a surfactant or polymer monolayer can be used to obtain information about the complex shear modulus of the monolayer [4], though the results are still controversial and a careful examination of the data must be performed for using particles as rheological probes.

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COST-1106

Temperature and Hydration Induced Phase Transitions in Starch: the Phase Diagram Approach

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Transitions in starch – water systems has been known for centuries. Still, until recently they were not understood on fundamental thermodynamic level. To investigate temperature and hydration induced transitions in starch we studied three starch systems: native potato starch, acid-hydrolysed starch and starch microspheres using a multi-method approach. Combination of optical microscopy, synchrotron X-ray scattering, sorption calorimetry and differential scanning calorimetry was used. For the first time, thermodynamically consistent phase diagrams of starch - water systems are presented. Such events as gelatinization, glass transition, sub-T_g transition and melting of freezable water were systematically analysed.

By constructing a detailed phase diagram for the potato starch-water system, we show that gelatinization can be interpreted in analogy with a eutectic transition. The phase rule explains why the temperature of the gelatinization transition is independent on water content. Furthermore, the melting endotherm observed in DSC represents a liquidus line; the temperature for this event increases with increasing starch concentration. Both the lamellar spacing and the inter-helix distance were observed to decrease with increasing starch content for starch concentrations between approximately 65 wt% and 75 wt%, while the inter-helix distance continued decreasing upon further dehydration.

Isothermal glass transitions were clearly seen in acid - hydrolysed starch and in cross-linked starch microspheres. In the former case the glass transition was followed by spontaneous crystallization, while in the latter case the cross links prevented crystallization.

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Wojtasz, J.; Carlstedt, J.; Fyhr, P.; Kocherbitov, V. Hydration and swelling of amorphous cross-linked starch microspheres. (Submitted)

Synthesis of biocompatible porous monolithic materials

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Rational design of porous monolith materials is nowadays a highly competitive field of research [1-4] In this context of generating complex architectures through a strong rational design, the concept of integrative chemistry [5] has emerged from the interface between bio-inspired approaches, general soft chemistry, including hybrid organic–inorganic chemistry, and the physical chemistry of complex fluids.

Herein, solid monolithic biocompatible macrocellular foams are synthesized by mineralizing the continuous phase of oil-in-water Pickering emulsions stabilized by hydroxyapatite nanoparticles. The concentrated emulsions act as templates for the sol–gel process [6]. They are obtained by taking advantage of the limited coalescence phenomenon occurring in emulsions stabilized by solid particles and leading to narrow drop size distribution [7]. After mineralization, the synthesized monolithic foams exhibit nearly monodisperse macroscopic voids (see figure).

Such a strategy [8] allows independent tuning of the macrocellular void diameters from 20 to 800 μm and the diameter of the windows connecting adjacent cells. With this process the surface of the macropores is covered with low temperature hydroxyapatite, which is known to be highly bioactive.

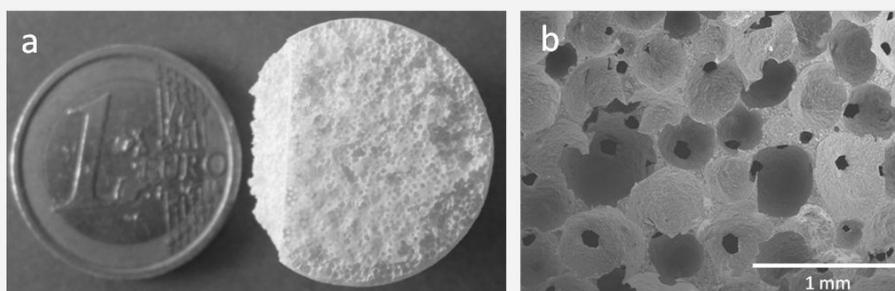


Figure: a) monolith b) final materials with controlled pores and window sizes

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Cobalt and titanium nanoparticle influence on mesenchymal stem cell mechanical properties

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Bone cells are often reported as being damaged by inflammatory responses due to wear particles originating from joint replacement devices. Wear particles initiates the immune response often causing osteolysis and aseptic loosening of the articulated implanted device. The wear particles can also have a toxic effect on the surrounding cells, especially on mesenchymal stem cells (MSCs). Damage to these cells effect the renewal of bone which may be harmful to the longevity of the device and the comfort of the patient. Generally, investigations on nanoparticle influence on mammalian cells are focused on the assessment of cell viability, cytokines release and gene up/down regulation. However, cell nanomechanical properties such as elasticity and turgor pressure have been shown to be involved in biological responses to both chemical or physical cues and therefore, wear particles induced changes in cell mechanical properties, could lead to further understanding of interactions between cells and nanoparticles.

We investigated the effect on cell elasticity and spring constant of MSCs cells when exposed to cobalt and titanium nanoparticles of different sizes for up to 3 days. AFM nanoindentation was carried out on multiple locations on each cell to determine the spatial variation of the mechanical properties whilst viability was assessed using flowcytometry. Elasticity and cell spring constant were estimated through fitting of different regions of the indentation curve. The results demonstrated that cells exposed to increasing concentrations of nanoparticles had a lower value of elasticity and spring constant without significant effect on cell viability. Cobalt induced grater effect than titatium and this is consistent with the general knowledge of cytocompatibility of the later; little influence due by the size was noticed.

This work demonstrates for the first time that metal nanoparticles originated from wear of orthopaedic devices do not only influence cell enzyme activity but also cell structure.

Biopolymer inspired formation of nanoporous calcium phosphate card house structures

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Calcium phosphates (CaP) are the major inorganic mineral components of vertebrate bone and tooth. In bone tissues the mineralization of CaP is induced by collagen with assistance of osteoblast under mild physiological conditions, i.e. at low temperatures (37°C) and pH 7.4. In order to mimic bone mineralization one has to understand the polymer-controlled CaP precipitation process in more detail.

Here we present a CaP precipitation procedure in presence of gelatin and chitosan. The results show that only in presence of both biopolymers a nanoporous card house structure is formed. Additionally experiments, i.e. polyelectrolyte titrations and Differential Scanning Calorimetric (DSC) investigations, indicate that gelatin-chitosan complexes located between the CaP platelets are responsible for the formation of such an open nanoporous structure.

After heating up the hybridmaterial to 600°C the polymer components are burned out, and supramolecular flower-like ball structures are formed, shown in Figure 1. FT-IR spectroscopy, powder diffractometry and high resolution TEM show that dicalcium and β -tricalcium phosphate crystals are formed. This means the chitosan-gelatin composite controls the mineralization process and take over the role of a spacer between the platelets during the heating process preventing a compactization of the platelets. The finally obtained nanoporous balls are of special interest as bone repair material.

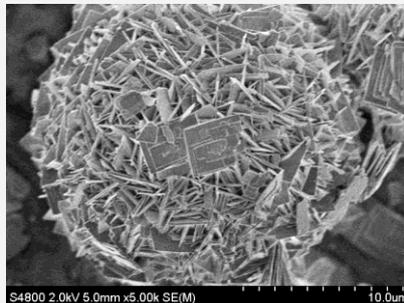


Figure 1: SEM micrograph of nanoporous CP card house structures

Bioimprinting Technology for The Removal of Blood Cancer Cells From Acute Myeloid Leukaemia Patients

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Bioimprinting technology has been recently developed to capture proteins, viruses and entire living cells via their structural and chemical information. Bioimprinting techniques can permanently capture an impression of biological samples into polymer surfaces with promising approaches for early cancer diagnosis [1], developing selective antimicrobial therapies and formulations [2]. Here we report a novel *in-vitro* approach for the removal of myeloblasts from peripheral blood samples utilizing a cell shape recognition technology. Due to size and shape differences between myeloblasts and normal white blood cells, myeloblasts represent an ideal target for bioimprinting.

In this work, we introduce the bioimprinting technology to replicate myeloblasts (ATCC) based on their surface information. Myeloblasts were inactivated with fixatives to preserve the structural and morphological information. Monolayers of fixed myeloblast cells were prepared by immobilisation on a polyelectrolyte pre-treated glass slides and partially protected by a film of glucose solution. Curable polymer (PDMS) was used to imprint the exposed part of the cell monolayer and was peeled off after curing. In this talk we will present the results of our myeloblast cell recognition experiments as a function of the cell concentration and surface coatings of the produced cell imprints. The results indicate that the cell imprinting technology can be used to capture the cells based on their shape and size. We demonstrate the selectivity of the cell imprints in retention of the cells of matching shape in a mixture with other cells. This technology is expected to find application in AML cell separation devices.

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Smart Polymeric Nanomaterials by ROMP

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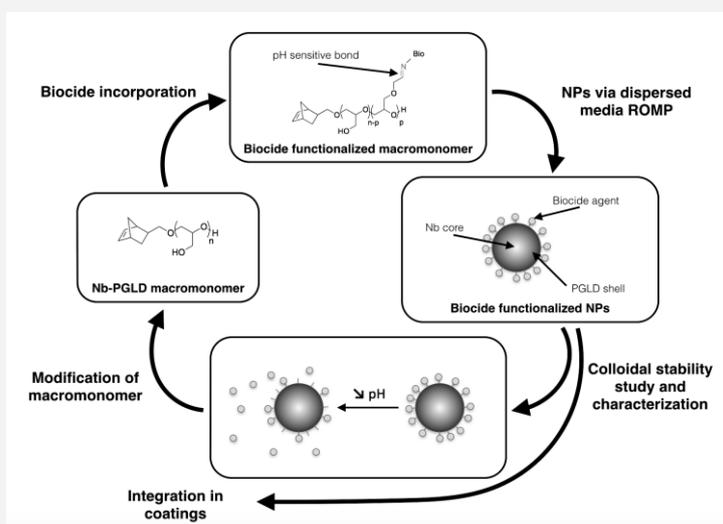
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Bacterial contamination on the surface of metal-based materials is a critical issue for their durability. Microbial populations, whether they are fungi or bacteria frequently produce organic acids during their development. Irreversible damage can therefore be observed due to corrosion. For the moment, this problem can only be addressed in a non-specific manner or using extremely harmful compounds. This project aims at developing a new system based on plurifunctional nanoparticles (NP) that deliver a biocide in a controlled manner. The trigger for the release is a decrease in pH, linked to the growth of microorganisms, leading to cleavage of the bond between the active molecules and the NP.

The NPs are obtained by the Ring-Opening Metathesis coPolymerization (ROMP) of norbornene (Nb) with an ω -norbornenyl-polyglycidol macromonomer (Nb-PGLD). The latter serves both as stabilizer for the preparation of the NPs either via dispersion or miniemulsion ROMP, and as loading loci for active molecules using the functional groups along the PGLD chains. The linear chains are obtained by a glycidol monomer protection-polymerization-deprotection strategy. This is followed by functionalization of the repeating units on the stabilizing chains to graft the biocide using an imine bond. By controlling the chemical and physico-chemical characteristics of this compound, it is possible to fine-tune the colloidal stability and the size of the NPs. By this technique, the ease of release and the efficacy of various antimicrobial agents against the development of various strains can be evaluated.

This type of triggered release system can aspire to be integrated in coatings, in order to fight the growth of microorganisms under long-term confinement conditions.



Sulfate-based anionic diblock copolymer nanoparticles for efficient occlusion within zinc oxide

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Occlusion of copolymer particles within inorganic crystalline hosts not only provides a model for understanding the crystallisation process, but also may offer a direct route for the preparation of novel nanocomposite materials with emergent properties. In the present paper, a series of new well-defined anionic diblock copolymer nanoparticles are synthesised by polymerisation-induced self-assembly (PISA) via reversible addition-fragmentation chain transfer (RAFT) aqueous emulsion polymerisation and then evaluated as crystal habit modifiers for the in situ formation of ZnO in aqueous solution. Systematic studies indicate that both the chemical nature (i.e. whether sulfate-based or carboxylate-based) and the mean degree of polymerisation (DP) of the anionic stabiliser block play vital roles in determining the crystal morphology. In particular, sulfate-functionalised nanoparticles are efficiently incorporated within the ZnO crystals whereas carboxylate-functionalised nanoparticles are excluded, thus anionic character alone is a necessary but not sufficient condition for successful occlusion. Moreover, the extent of nanoparticle occlusion within the ZnO phase can be as high as 23 % by mass depending on the sulfate-based nanoparticle concentration. The optical properties, chemical composition and crystal structure of the resulting nanocomposite crystals are evaluated and an occlusion mechanism is proposed based on the observed evolution of the ZnO morphology in the presence of sulfate-based anionic nanoparticles. Finally, controlled deposition of a 5 nm gold sol onto porous ZnO particles (produced after calcination of the organic nanoparticles) significantly enhances the rate of photocatalytic decomposition of a model rhodamine B dye on exposure to a relatively weak UV source.

Release Characteristics of Payloads Encapsulated in Nanocontainers via Osmotic Pressure and Swelling

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The controlled swelling of polymer membranes plays an important role in controlled drug delivery, separation process, and food processing [1]. Osmotic pressure of salts induces pressure differences between interior and exterior environments of systems enclosed by a polymer shell. Swelling arising from these pressure differences governs materials (e.g. water) flux through semipermeable membranes [2].

In particular, nanocapsules, which are defined as a liquid core surrounded by a polymer membrane, are one of the most well-known controlled release systems [3]. Although considerable efforts have been devoted to prepare functional nanocapsules that exhibit a structural transition in response to small changes in environmental conditions [4, 5], there are still considerable demands for new methods to control permeability.

In this study, we programmed the release profile of the encapsulated payload by controlling the concentration and the nature of the co-encapsulated salts. Swelling induced by the co-encapsulation of salts has been found as the responsible mechanism for the acceleration of the payloads release through the shell. We also show how a crosslinker can be effectively used to achieve a desired release profile when the burst release of the payload (e.g. salt) is not favourable.

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Hybrid colloidal particles used as template for the fabrication of gold nanocages

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Gold nanoparticles and more especially gold nanocages are a subject of intensive research for their fascinating optical properties. Recently, we have developed a new method to produce gold nanocages using hybrid silica/polystyrene particles with polyhedra shapes as template.

First, using a combination of emulsion polymerization and inorganic surface chemistry complex geometries, such as triangles, tetrahedra or octahedra were synthesized [1]. Then, we succeeded in promoting the growth of the silica core. While growing, the pristine silica surface conforms to the shape of the polystyrene nodules [2]. Finally, using electroless gold plating, gold nanocages with a controlled number of holes were obtained [3].

These gold nanocages offer the unique capability of creating new nano-objects suitable for many applications such as sensing, metamaterials, photonics, etc.

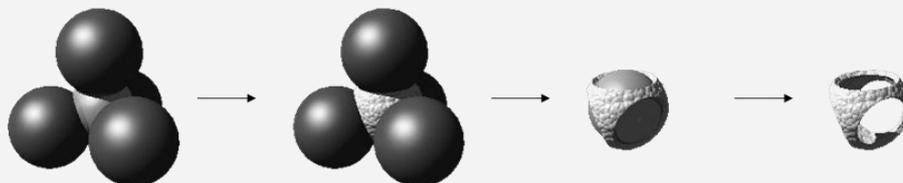


Fig. Schematic representation of gold nanocages fabrication. 1) silica growth onto a hybrid tetrahedron; 2) deposition of gold onto the pristine silica; 3) dissolution of the polystyrene nodules; 4) dissolution of the silica core.

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Multi-functionalized Magnetite/Gold Nanoparticles for Medical Purposes

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In this work, we investigate a route towards the synthesis of multi-functionalized nanoparticles for medical purposes. The aim is to produce magnetite/gold (Fe₃O₄/Au) nanoparticles capable of carrying simultaneously an antitumor drug and a selected antibody chosen so as to improve specificity of the drug vehicle. The procedure included, firstly, the preparation of Fe₃O₄ cores coated with Au nanoparticles: this was achieved by using initially the layer-by-layer technique in order to coat the magnetite particles with a three polyelectrolyte (cationic-anionic-cationic) layer [1].

The resulting nanoparticles benefit from the magnetic properties of the magnetite and the robust chemistry and the biostability of gold surfaces. Subsequently, the Fe₃O₄/Au nanoparticles were functionalized with a humanized monoclonal antibody, bevacizumab, and a chemotherapy drug, doxorubicin [2]. Taken together, bevacizumab enhances the therapeutic effect of chemotherapy agents on some kinds of tumors. In this work we first discuss the morphology of the particles and the electrical characteristics of their surface in the successive synthesis stages. Special attention is paid to the chemical stability of the final coating, and the physical stability of the suspensions of the nanoparticles in aqueous solutions.

We describe how optical absorbance and electrokinetic data provide a follow-up of the progress of the nanostructure formation. Additionally, the same techniques are employed to demonstrate that the composite nanoparticles are capable of loading/releasing doxorubicin and/or bevacizumab (Figure 1). **COST CM1101 working group: WG3**

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Aknowledgments

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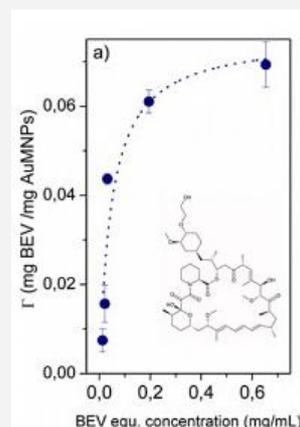


Figure 1. Adsorption density of BEV on AuMNPs, as a function of antigen equilibrium concentration.

Fluorescence Quenching of Poly(2-methoxy-5-propyloxy sulfonate phenylene vinylene) by the Heme Protein Cytochrome c

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COST WG3

Water dispersed conjugated polymers are highly sensitive to a tiny quantity of analyte and have found utility in the fabrication of biosensors [1]. Water soluble derivatives of poly(p-phenylenevinylene (PPV) are of particular interest because of their thermal stability and easily tunable optical and electronic properties [2]. Among these polymers, poly-5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene (MPS-PPV) has attracted attention as potential biological and chemical sensor [3].

We investigate the mechanism of fluorescence quenching of MPS-PPV by the heme protein cytochrome c Fe(III). Experiments with ferrous cytochrome and ferric cytochrome c have been carried out and we found that the Stern-Volmer constant is similar independently of the oxidative state of the iron which seems to indicate that photoinduced electron transfer between the iron atom of the protein cyt c and the conjugated polymer does not play any role on the fluorescent quenching.

The active site of the cytochrome c is constituted by a porphyrin ring whose precursors are protoporphyrin IX and hemin. In order to elucidate if the fluorescence quenching is provoked by the porphyrin ring of the protein we have investigated the fluorescence quenching of the polymer by these two molecules. Our results suggest that the quenching mechanism is based on the resonance energy transfer between the electron-rich MPS-PPV and the electron-deficient porphyrin ring of cytochrome c. Furthermore, this result is supported by the quenching observed using the 5,10,15,20-Tetrakis-(4-trimethylammonio-phenyl)-porphyrin-tetra-(p-toluenesulfonate).

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Biocompatible theranostic oil-core nanocarriers as fluorescent markers for bioimaging and cancer therapy

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The present studies point out to viability of the development of a combined therapeutic and imaging (theranostic) modalities platform by encapsulating together hydrophobic cytostatic agents and luminescent labeling QDs within the oil-core compartment of specially engineered nanocapsules that would allow investigation of penetration and localization of the multifunctional nanocarriers in various cancer cells. This strategy is based on encapsulation of colchicine (Col, cytostatic drug) and CdSe/ZnS core/shell quantum dots (QDs, fluorescent biomarker) in oil-core nanocarriers prepared via the emulsification/solvent-evaporation method. Poloxamer 403 was applied as the polymer component, Cremophor EL as the nonionic surfactant and mineral oil, oleic acid or silicone oil were used as the oil phases. Dynamic light scattering (DLS) and ζ -potential measurements confirmed the nanocapsule diameter below 200 nm and physical stability, while transmission electron microscopy (TEM) and atomic force microscopy (AFM) its morphology and shape. The potential of the encapsulated QDs and Col for fluorescent imaging and anticancer therapy was evaluated in cytotoxicity studies (time-dependent MTT assay) as well as in imaging of intracellular localization, accumulation and distribution of the theranostic cargoes delivered to well-characterized human cancer cell lines - doxorubicin-sensitive breast (MCF-7/WT) and lung epithelial (A549) - as well as on normal human umbilical vein endothelial (HUVEC) cells, performed by confocal laser scanning microscopy (CLSM). The resulting nanotheranostics are shown to exhibit time-dependent anticancer effect of Col against MCF-7/WT and A549 cells, strong two-photon induced luminescence upon excitation in the NIR optical transmission window spectral range and retain excellent stability when stored (in the dark conditions) up to 30 days, making them ideal agents for bioimaging and drug delivery.

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Impregnation by salts and wood swelling with salts: ion specific kinetics and thermodynamic affects

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Wood is a cellular, heterogeneous, anisotropic, hygroscopic material of colloidal size ultra-structure: distances between cellulose nanofibers is between 1 and 4 nm typically: in this intercrystalline gap, the complex fluid is a concentrated aqueous solution of hemi-cellulose and lignin.

At the colloidal scale, water uptake is controlled by molecular forces like entropy, hydrogen-bonding of polysaccharides to cellulose nanocrystals, and hydration forces. Thus, the attempt to control the behaviour of wood fibres upon swelling represents a major technological challenge, that requires knowledge of the equation of state of the material. Known approaches (impregnation treatments, chemical modifications,..) able to increase wood properties should be rationalized in terms of water sorption isotherms.

In this paper, we describe sorption of different salts within the wood cell walls, occurring upon soaking from solutions of known osmotic pressure. We distinguish between transient and equilibrium states, and examine the consequences on wood swelling and variations of mechanical properties. These impregnation experiments were conducted following *in-situ* the volume variation of wood tissues at constant mechanical stress using home-build micro-tensile stages. The impregnated materials were characterised using water sorption, as well as X-Ray scattering and electron microscopy techniques. A first attempt of predictive modelling including electrostatic terms at colloidal scale in the master equation (1) will be given.

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Surfactants toxicity towards skin

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The toxicity of surfactants is an issue for the formulation of cosmetic products. Mild (low irritant) surfactants are preferred, in particular in body care formulations and shampoos and concentrations are limited. The selection of mild surfactants relies on empirical knowledge and general rules that often received poor scientific support. As example, ionic surfactants are more irritant than nonionic, or micelles cause irritancy whereas surfactants having high CMC are irritant, which is contradictory.

Relationships between physicochemical properties and skin toxicity have been tracked over a large series of surfactants covering a wide range of properties. A comprehensive dataset of MTT and LDH cytotoxicity measurements and detection of inflammation markers IL-1 α and IL-8 was correlated with several descriptors of surfactant properties (CMC, HLB, chemical structure, phase diagrams...) through a Principal Component Analysis. Surfactants could be very clearly split into two classes, irritant and mild. A surfactants descriptor of statistical relevance in PCA was the order parameter of the surfactant estimated from the phase diagrams [1].

The physicochemical origin of irritancy by surfactants was investigated through measurements of the organization of skin lipids by IR-ATR, skin surface free energy and extraction of skin lipids. Among the various assessed mechanisms: detergency causing extraction of skin lipids, surfactants absorption causing disorganization of lipids in the *stratum corneum*, adsorption of surfactant modifying the free energy of the skin surface, it was concluded that the main cause of skin irritancy was the damage of the skin barrier function by fluidization of the lipids in the *stratum corneum* [2].

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How X-rays, light and neutrons help to understand presbyopia

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Flexibility is an important feature of the eye lens, allowing it to properly adjust focus. With age however, the stiffness of the core of the eye lens increases,^{1,2} thus causing a gradual loss of the ability to change focus, a condition known as presbyopia. In order to elucidate the potential molecular origin of this hardening of the eye lens we have started a systematic investigation of the proteins that make up the eye lens, the so-called crystallins.

Here we present an experimental study of the structural and dynamic properties of solutions of two of the individual constituents of the eye lens, α - and γ B-crystallin, involving various types of scattering methods. These proteins are known to behave like hard spheres (α -crystallin) and short-range attractive particles (γ B-crystallin). Small angle X-ray scattering, together with static and dynamic light scattering, yields information on the direct protein interactions, as well as their structural and collective diffusive properties. To gain insight into the diffusive behaviour of the proteins at the local length scale relevant for protein interactions, we complemented these techniques with quasielastic neutron scattering, using the neutron spin echo method.

Studying protein concentrations up to those present in the lens, we are able to identify different arrest scenarios as possible factors underlying the gradual hardening of the core of the eye lens, and thus the formation of presbyopia.

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Self-Assembled DNA Nano-Networks in Solution and on Surfaces

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Single stranded DNA (ssDNA) is a biopolyelectrolyte that can serve as a polymeric material which self-assembles into higher-ordered structures. Its molecular recognition properties, the easy synthesis, the broad range of strand lengths accessible and its nanoscale dimensions make ssDNA an exciting material for nanofabrication.

We synthesized two complimentary ssDNA strands (PolyA and PolyT) that, when combined, self-assemble into a random network. The network structure was studied by AFM imaging after drying very dilute solutions, where we addressed in particular the question of how to orient these networks by directed flow. Whether the network formation takes place in solution or only during the immobilization process, cannot be ascertained by AFM imaging. Additional Fluorescence Correlation Spectroscopy (FCS) measurements show a significant increase of the decay time of a mixed PolyA and PolyT sample compared to that of samples containing only ssDNA. This observation proves that aggregation of ssDNA into supramolecular structures occurs already in solution.

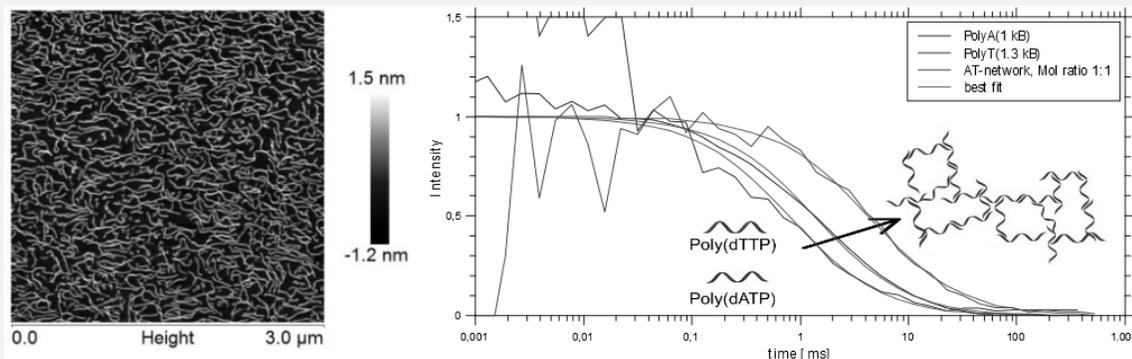


Figure 1: Left - AFM image of a self-assembled DNA network on a surface. Right - FCS curves, showing an increased decay time upon network formation in solution.

Furthermore, we studied the effect of different system parameters on the network formation on surface and in solution, including ssDNA length, concentration, and ionic strength.

To understand the effects and parameters that control ssDNA self-assembly is important for the actual use of DNA networks in nano devices and should allow the fabrication of very well defined nanostructures.

Off-equilibrium surface tension in colloidal and polymer suspensions

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Surface tension between immiscible fluids is a well-understood and well-characterized phenomenon. By contrast, much less is known about the effective, off-equilibrium surface tension that arises when a (transient) interface is created between miscible fluids. This effective surface tension plays a key role in many driven phenomena, from jetting and drop formation and coalescence to precipitation and deposition, as it was already recognized more than 100 years ago by Korteweg [1]. However, experimental investigations in this field remain scarce and the theoretical predictions by Korteweg have not quantitatively tested so far, to the best of our knowledge. We present a thorough experimental investigation of the Saffman-Taylor instability arising when a simple fluid (the solvent of a colloidal or polymer suspension) is pushed through a miscible, more viscous one (the colloidal or polymer suspension itself). We show [2] that the resulting interface pattern can be accounted for by the non-linear rheological properties of the suspension and an effective surface tension. By measuring the effective surface tension for suspensions at a variety of polymer volume fractions, we successfully test Korteweg's theory for free and cross-linked polymer suspensions. We moreover find that the effective surface tension increases with the size of polymers, a surprising result at odd with the typical behavior in atomic or colloidal systems at equilibrium, where the surface tension usually decreases as the squared particle size. Finally we present new data on the effective surface tension between suspensions of hard, compact particles and their own solvent showing that polymers and hard particles exhibit vastly different effective surface tension properties. We discuss this surprising result in view of available models for interfacial stresses.

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Scattering and spectroscopic study on hydration and phase behavior of aqueous alcohol ethoxylate and methyl ester ethoxylate

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Pentadeca oxyethylene monododecyl ether ($C_{12}E_{15}$), classified into a conventional alcohol ethoxylate (AE), and methyl ester ethoxylate ($C_{12}MEE$) synthesized from natural plant-based oils having a methoxy terminal group in a hydrophilic chain, exhibit fairly different phase behavior. AE produces liquid crystalline (LC) phases at W_S (surfactant weight fraction) > 0.4 whereas MEE retains a liquid (disordered) phase in an extremely wide concentration range ($W_S < 0.7$) at ambient temperature. This can be a great advantage of MEE for the formulation of a highly concentrated liquid detergent, in addition to its significantly higher detergency.

Here, we discuss effects of the end-caps on the hydration and phase behavior. To clarify structure and dynamics of AE and MEE in water, we used small angle X-ray scattering (SAXS), dynamic light scattering (DLS), dielectric relaxation spectroscopy (DRS). Static structure factor deduced by a generalized indirect Fourier transformation (GIFT) analysis of the SAXS data and effective hydration number evaluated by DRS revealed that hydration water molecules, exhibiting 3-4 times slower collective reorientational dynamics than bulk water, contribute to the excluded volume of the micelles. MEE shows smaller hydration number and the consequently lower excluded volume than AE, due to the blocked terminal hydrogen-bond donor/acceptor site. The collective diffusion constant (D_c) of the AE micelles determined by DLS monotonously increased in the entire micellar phase region as expected for a pseudo hard sphere. The MEE micelles exhibit nearly identical D_c values at low W_S , but show a rapid slowdown in $W_S > 0.2$. The observation demonstrates the onset of elongation of the micellar structure in aqueous MEE. We also report dynamical aspects of hydration water in the LC and highly concentrated liquid phases.

Uniform deposition of particles on absorbing gels

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A drying drop containing solid particles, such as coffee, leaves a ring stain resulting from the accumulation of the particles near a contact line [1]. In many industrial applications such as printing, coating or biological microtechnologies, these inhomogeneities must be avoided.

To suppress the coffee stain effect, different strategies have been developed. A physicochemical route consists in adding surfactant that reverses the internal flow with a Marangoni effect [2]. This suppression has also been observed in mixtures of spherical and ellipsoidal particles, which introduce shape-dependent capillary interactions [3]. All of these strategies involve the liquid phase or the particles, and are combined with evaporation to remove the solvent.

In the present work, we propose to substitute the drying by absorption in hydrogels to extract the solvent of a colloidal drop. We study the deposition mechanisms of micrometer-sized particles on the surface of swelling hydrogels. To the best of our knowledge, we show for the first time that the particle deposition on these gels is homogeneous. Using fluorescence microscopy coupled with particle tracking techniques, we record the flow field inside the droplet and analyze the particle deposition mechanism. We rationalize our findings with a theoretical model for the absorption and the particle deposition dynamics that enables the measurement of the diffusion coefficient in the gels.

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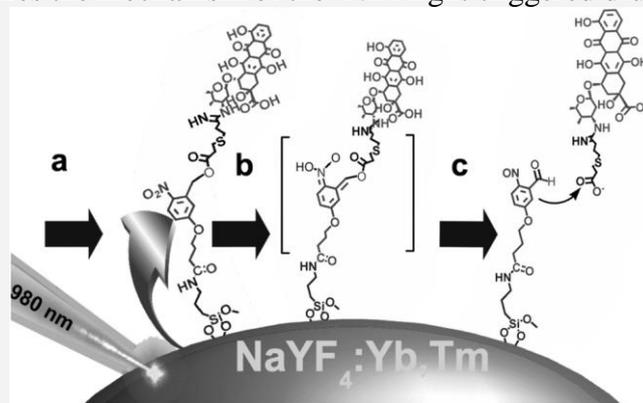
Remote Delivery of Doxorubicin through NIR Light Responsive Up-Conversion Nanoparticles

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In this work we have developed a phototriggered drug delivery system based on UCNPs@SiO₂. These nanoparticles present upconversion photoluminescence, which is a unique type of Anti-Stokes fluorescence in which the excitation wavelength is higher than the emission wavelength. In a typical upconversion process, two or more low-energy photons can be converted into a high-energy photon. This process can occur in rare-earth doped NaYF₄ upconversion nanoparticles (UCNPs), which can absorb NIR light at a wavelength of 980 nm and emit UV-Vis photons. The UV-Vis emission can be combined with photodegradable molecules to create light responsive anchoring points that could release the drug upon the irradiation with UV light. In our system the photodegradable molecules anchored on the surface of the nanoparticles were used to link Doxorubicin (Dox), a potent cytotoxic drug. The NIR-light-triggered drug release rendered an “on-off” delivery system that could be used in biomedical applications. The scheme 1 summarizes the mechanism of the NIR-light-triggered drug delivery system.



Scheme 1. After absorption of 980 nm CW laser light, the UCNP would emit photons in the UV region (345 nm and 365 nm), which could be absorbed by the *o*-NBA molecules anchored on the surface of the UCNPs. The absorption of these photons could initiate the molecule degradation and release the Dox anchored on it.

This drug delivery system, with an “on-off” switch mechanism triggered by NIR light, was tested *in vitro* with HeLa cells and showed great potential to deliver the drug in a specific tissue with a remote signal. The present study provides a new development of photosensitive materials of biomedical interest.

Polyelectrolyte nanocapsules – promising drug delivery system

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Cancer remains one of the biggest cause of death in humans, therefore, great efforts have been undertaken to treat it. However, a major problem that limits the success of many anticancer agents is an inability to selectively target tumor cells and tissues; instead, such agents also affect healthy tissues and organs. The most promising approach to prevent that side effect is a drug targeting. The use of polymeric nanocapsules in targeted drug delivery has large expectations since nanoscale materials interact effectively with biological systems and may overcome many intractable health challenges. The layer-by-layer adsorption of charged species is considered as a convenient method to obtain multilayer nanocapsules' shells on colloidal cores. Therefore, the aim of our work was to develop the method of encapsulation of anticancer drugs in polyelectrolyte nanocapsules and their further surface modification for passive and active targeting of cancer cells. Nanocapsules were prepared by direct encapsulation of emulsion droplets containing anticancer drugs in polyelectrolyte multilayer shell formed by the layer-by-layer technique with bio-acceptable polyelectrolytes: Poly(L-Lysine) and Poly(Glutamic acid). The average size of the obtained capsules ranged from 60–120nm. Surface of obtained capsules were modified by pegylation for passive targeting and further by immobilization of targeting ligands for active targeting. The copolymers with PEG chains grafted to a polyelectrolyte backbone were used to immobilize PEG on polyelectrolyte capsules. In order to verify the cytotoxic effect of nanocapsules on mouse colon cancer, mouse mammary carcinoma and mouse colon adenocarcinoma cells the MTT and LDH assay were performed. Results show high activity of the nanoencapsulated anticancer drugs and demonstrate that such drug nanocarriers might serve as a novel, promising therapeutic agent for the anticancer therapy

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W/O microemulsions as bioactive carriers: experimental and theoretical approach

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W/O microemulsions are colloidal self-assembled dispersions that may be used as vehicles of various bioactive molecules. Characterization of their structure and dynamics is a key factor for any further applications. In particular when bioactive molecules are encapsulated, it is important to determine their localization within the various microdomains of the system and the eventual structural alteration they may induce.

In the present work biocompatible W/O microemulsions were formulated using small amounts of lecithin/monoglycerides (L/MG) to disperse an aqueous phase in medium chain triglycerides (MCT). Within the aqueous droplets hydroxytyrosol (HT), a dominant hydrophilic antioxidant of Extra Virgin Olive Oil was effectively solubilised. These microemulsions in the presence and absence of HT were structurally characterized using Dynamic Light Scattering (DLS) and Electron Paramagnetic Resonance (EPR) spin probe techniques [1].

To confirm the experimental findings, W/O microemulsion nanostructure's studies were carried out by means of Coarse-Grained Molecular Dynamics (CGMD) simulations. In general, CGMD simulations allow significant computational cost reduction, a critical prerequisite when studying phenomena such as reverse micelle formation, which span the time scale of microseconds.

The Martini force field [2] has been successfully employed for analogous systems [3] and here it has been utilized in the description of three representative model systems, namely a) MCT - L/MG, b) MCT-L/MG-water and c) MCT-L/MG-water-HT, in accordance to their experimental counterparts. Generally, CGMD simulations provided further insight in the shape, size and self-assembly characteristics of the system under study.

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Toward synthetic photosystem I for biotechnological applications

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Low cost biotechnological processes have attracted much attention due to their high selectivity and shortened synthetic routes. Fewer by-products are generated, thus downstream processes can be simplified and purification steps are avoided. Enzymes are able to create chiral centers by transferring hydrides to desired substrate in a stereoselective fashion. Biological hydrides, associated with dehydrogenase enzymes in natural reduction processes, are very expensive. Therefore, their regeneration is of great interest for the development of low-cost biotechnological processes.

While natural and synthetic enzymes need a sacrificial hydride donor to carry out the reduction of nicotinamide adenine dinucleotide (NAD⁺). Natural photo-systems create hydrides from photo-generated electrons, and protons extracted from water. Carbon-nitride (C₃N₄) and its hybrids are photo-active semi-conductors widely known for their range of energy related catalytic application and notably suitable for the hydrogen evolution reaction.^[1] We could recently show that they are also efficient hydride donor for the activation of synthetic enzymes.^[2] The next generation of synthetic enzymes should mimic natural photo-systems and forms hydrides equivalents from water using light energy.

We synthetically reconstitute a natural photo-system by using photo-generated electrons from C₃N₄ for the reduction of NAD⁺ to the bioactive 1,4-NADH. A Rhodium based inorganic complex, directly coordinated at the edge of colloidal suspended C₃N₄ particles, is able to harvest photo-generated electron and selectively produce 1,4-NADH. Its bio-availability being further demonstrated with the enzymatic reduction of pyruvate to L-lactate. Our hybrid bio-inspired Frankenstein catalyst mimics natural photo-systems, it is a first step toward the development of entirely synthetic photosystems. Synthetic strategies and first catalytic performances will be shown and discussed in the context of biotechnological applications.

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Hyaluronan – Pluronic hydrogels: influence of the polyelectrolyte chain conformation on the structural distribution of micelles.

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In the medical field and especially for cancer treatment, intensive researches are performed to deliver the drug at the right position allowing reducing dose and side effects. The poor solubility in biological fluids of most of the approved drugs obliges to encapsulate them into carriers. The triblock copolymers Pluronics are bio-compatible and are stealth carriers [1]. Hyaluronic acid (HA) is a natural polyelectrolyte largely found in the body and currently investigated as a target-specific material because many malignant cancer cells overexpress HA receptors. Thus, Hyaluronan-Pluronics complexes may provide an interesting alternative for drug encapsulation.

The aim of the study is to characterize the structure of HA – Pluronic (F127) assemblies as a function of different parameters such as concentration, ionic strength and temperature. Combined small angle x-ray and neutron scattering demonstrate that HA does not modify the size and shape of the individual micelles. In pure water, the spatial distribution of micelles is not affected by the polyelectrolyte but in presence of salt, the formation of small micelle clusters with a finite size is observed. The cluster size increase with the length of the polyelectrolyte chain. In such nonionic / charged system, hydrogen bonds play an important role [2]. The change of the polyelectrolyte chain conformation (from elongated to more globular) induced by the screening of the electrostatic interactions in presence of salt is the motor of the clustering. Two hypothesis will be discussed: either the HA drags along and bring closer the micelles linked to its backbone or a nano-size phase separation occurs.

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Adhesion of Living Patchy Colloids to Surfaces

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The physics governing the adhesion of bacteria on surfaces is important for understanding biofilm formation [1,2]. This ubiquitous form of surface colonisation starts with just a few adhering bacteria [3]. However, to date, the understanding of the conditions and interactions involved in such initial surface adhesion remain incomplete, with many contradictory details in the literature. We have quantified the adhesion of *Escherichia coli* bacteria to treated glass surfaces. Using particle tracking algorithms adapted for rod-shaped bacteria, we follow the positions and orientations of bacteria close to the surface and distinguish between individual cells that are swimming, diffusing, or stuck. By comparing various strains of *E. coli*, we reveal a significant variation in the surface adhesion properties of bacteria within a single clonal population. Our results demonstrate that quantitation on the single-cell level is crucial for further progress in this field.

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Polysaccharide multilayer capsules as a carriers of bio-active hydrophilic compounds

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Multilayered capsules are formed through a subsequent layer-by-layer adsorption of a pair oppositely charged polysaccharides (chitosan and alginate) onto oil emulsion drops at low ionic strength [1]. The formation of the (O/W) emulsion stabilized by lecithin and the first adsorbed chitosan layer is performed according the procedure proposed by Calvo et al. [2]. The overcompensation of the surface charge and the evolution of a hydrodynamic thickness after each deposition step is studied by using dynamic light scattering method. The experimental results indicate formation of thick adsorbed layers and almost linear film growth regime. The produced (CHI/Alg)_n film was impregnated with positively charged hydrophilic compound (caffeine). The experimental results showed that the electrokinetic charge of the capsules decreases with increasing concentration of the caffeine in the emulsion due to the partial compensation of negative charge of the film.

The fraction of the condensed counterions near to the polyion surface which do not release upon the adsorption and the number of the adsorbed chitosan molecules in the first adsorbed layer are determined on the basis of theory of the counterion condensation of strong polyelectrolytes adsorbed on the weak charged surface [3]. The stability of the emulsion is analyzed according to the approach proposed by McClements [4]. The experimental value of the concentration of polyelectrolyte that can ensure the overcharging of the surface charge and stabilization of the system is very close to the theoretical one. These results shown that with similar calculation can to predict the effect of the degree of acetylation and/or molecular weight of chitosan on the stability and electrical properties of charged nanocapsules at low ionic strength.

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Functionalization of Cellulose through its Mineralization

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Cellulose fibrils are very appropriate for functionalization via the mineralization by methods developed in nanochemistry. Here they serve as a template for the preparation of superhydrophobic, photocatalytic and self-cleaning materials by the sol-gel chemistry. To form a superhydrophobic coating, cellulose was mineralized with the help of a new biocompatible silica precursor in aqueous solutions at ambient conditions. Fibrils thus treated could work as an efficient oil absorbent, removing spills from a water surface. Titania (TiO₂) coating was formed by another new route. It consisted in regulation of the mineralization through limited hydration of polysaccharide in nonaqueous media. This allowed obviating the common precipitation of titania after a precursor addition into aqueous or water-containing solutions. When titania precursor was admixed in nonaqueous media with cellulose, it was involved into the instant hydrolysis and following condensation reactions where contacting with the hydrating water going to work as a reaction center. This resulted in TiO₂ formation mainly on cellulose fibrils. It was treated at various temperatures to transfer titania into a crystalline state. Cellulose demonstrating significant self-cleaning ability under the outdoor sunlight irradiation was prepared at the moderate conditions (80°C). The polysaccharide template was also removed by calcination or carbonized that resulted in novel materials with crystalline titania. It was possible to regulate the ratio of anatase to rutile as well as dimension of nanocrystals. Some of prepared samples had a photocatalytic activity comparable with commercial photocatalysts..

Single Particle Dynamics in the Smectic-A Phase of a Guest-host System of Viral Rods

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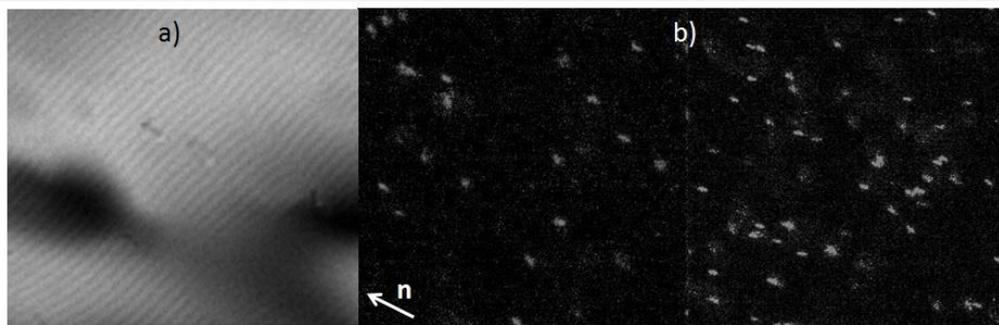
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Fd viruses have been used as model system of colloidal particles. In aqueous solution they form several lyotropic liquid crystalline mesophases, in particular Smectic phase due to their high monodispersity in size. They can also be easily genetically modified to obtain mutants with different physical properties (length, flexibility, surface charge...). In this work, we study the self-diffusion at single particle level in the Smectic-A phase of rod-like viruses with high aspect ratio ($L/D > 100$): the mutants fdY21M and M13KO7¹. The experimental system consists in a host Smectic-A mesophase formed by the stiff fdY21M² in which longer M13KO7 virus is added as a guest. The ratio between both particle lengths is 1.3 (L_{M13KO7}/L_{fdY21M}) and as a consequence the guest particles are rejected from the Smectic layers and exhibit anormal diffusion. Direct visualization and tracking by fluorescence microscopy is performed thanks to the presence of labeled viruses. For fdY21M hopping-type diffusion with an amplitude of one rod-length is observed between layers as it was already reported for the Smectic phase^{3,4}, and fast diffusion of M13KO7 has to be quantified by measuring the diffusion coefficients. With time, segregation of guest particles is observed confirming the non-accommodation in the host Smectic layers and therefore their location in defects.



a) Optical differential interference contrast (DIC) picture of host fdY21M Smectic phase. b) Fluorescence microscopy images of M13KO7-dylight550 (left) and fdY21M-Alexa488 (right) where the ratio between labeled virus and non-labeled virus is $1:10^5$. Images of both labeled virus are taken at the same time covering the same field of view with fast acquisition times.

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Specific salt effects on thermophoresis of charged colloids

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Recent experiments show that the thermally driven motion of charged colloids is to a large extent determined by the electrolyte Seebeck effect [1, 2, 3]. The electric double layer responds to a non uniform temperature through several mechanisms, resulting in a significant thermocharge and transport to the hot or to the cold side [4]. Here we discuss the Soret effect of charged polystyrene particles as a function of temperature and electrolyte composition [3]. As a main result we find that the Soret coefficient is determined by charge effects, and that non-ionic contributions are small, contrary to protein thermophoresis. Our thermal field-flow fractionation data lead us to the conclusion that the Soret effect originates from diffusiophoresis in the salt gradient and from the electrolyte Seebeck effect, both of which are specific-ion effects.

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Brownian diffusion of a partially wetted colloid

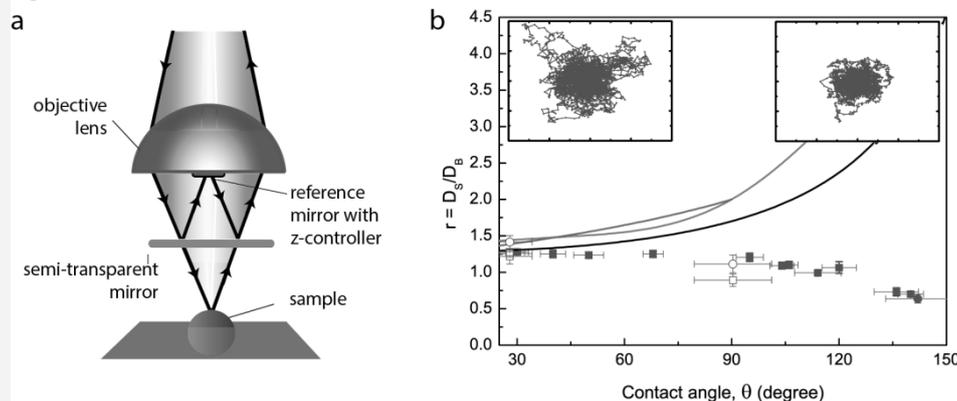
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The dynamics of colloidal particles at the interface between two fluids plays a central role in biofilms formation [1], water remediation [2] or interface driven assembly of materials [3]. Common intuition corroborated by hydrodynamic theories [4] suggests that such a dynamics is governed by a viscous force lower than the one observed in the more viscous fluid.

In this contribution we study the Brownian motion of micrometric spherical and ellipsoidal colloids at a flat air-water interface. We control the immersion depth in water, which is also measured in situ by a homemade Vertical Scanning Interferometry [5] (fig.1a), and the ellipsoid aspect ratio [6]. The translational and the rotational dynamics are followed by particle tracking. Counter-intuitively, and against all established models, we show experimentally that particles straddling a fluid interface feel instead an unexpectedly large viscous drag, even larger than the one measured in water (fig.1b).



To explain this extra dissipation we devise a model considering the contribution of thermally activated fluctuations of the interface at the triple line. Such fluctuations couple with the lateral movement of the particle via random forces that add to the ones due to the shocks of surroundings molecules. Fluctuation-dissipation theorem allows obtaining the extra friction associated to this additional mechanism. The fitting values of the total friction are discussed in term of the typical scales of particle surface heterogeneities and of surface capillary waves.

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The solvation of anions in propylene carbonate

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The solubility of some univalent potassium salts was measured in three different cyclic carbonates (ethylene, propylene and glycerol) at different temperatures.

From the solubility measurements, the thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 of solution were determined. From these, the enthalpy and entropy of solvation were calculated and discussed in terms of the Born model.

The open question of whether specific ion (Hofmeister) effects are restricted to hydration peculiar to water is resolved. As for water the effects are due to solute (ion, dipolar) induced solvent structure not accounted for by electrostatic forces.

Structural and Microscopic Relaxations in a Colloidal Glass

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The aging dynamics of a colloidal glass has been studied by multiangle Dynamic Light Scattering, Neutron Spin Echo, X-ray Photon Correlation Spectroscopy and Molecular Dynamics simulations. The microscopic (fast) and structural (slow), relaxation processes have been investigated in an unprecedentedly wide range of time and length scales covering both ergodic and nonergodic regimes. The microscopic relaxation time remains diffusive at all length scales across the glass transition scaling with wavevector Q as Q^{-2} . The length-scale dependence of structural relaxation time changes from diffusive, characterized by a Q^{-2} -dependence in the early stages of aging, to a Q^{-1} -dependence in the full aging regime which marks a discontinuous hopping dynamics. Both regimes are associated with a stretched behaviour of the correlation functions. We expect these findings to provide a general description of both relaxations across the glass transition.

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Foamed drinks as powerful tool to increase gastric volume and reduce appetite

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Background: Compared with nonaerated, isocaloric controls, aerated foods can reduce appetite throughout an entire dieting day. Increased gastric volumes and delayed emptying are possible but unexplored mechanisms.

Objective: We tested the hypothesis that aerated drinks (foams) of differing gastric stability would increase gastric distension and reduce appetite compared with a control drink.

Design: In a randomized, balanced, crossover trial, 18 healthy male participants consumed the following 3 skimmed-milk-based test products (all 110 kcal): 2 drinks aerated to foams by whipping (to 490 mL), one drink which was stable in the stomach [stable foam (SF)], and one drink which was less stable in the stomach [less-stable foam (LSF)], and a nonaerated drink [liquid control (LC); 140 mL]. Over 4 h, stomach contents (foam, air, and liquid) were imaged using magnetic resonance imaging (MRI), and self-reported appetite ratings were collected and quantified by the area under the curve or time to return to baseline (TTRTB).

Results: Compared with the LC, both foams caused significantly increased gastric volumes and reduced hunger (all $P < 0.001$). Compared with the LSF, SF further produced a significantly slower decrease in the total gastric content ($P < 0.05$) and foam volume ($P < 0.0001$) and a longer TTRTB (197 compared with 248 min, respectively; $P < 0.05$), although the hunger AUC was not statistically different. Results for other appetite scales were similar.

Conclusions: With this MRI trial, we provide novel insights on the gastrointestinal behaviour of aerated drinks measuring separate volumes of foam, liquid, and air layers in the stomach. Appetite suppression induced by foams could largely be explained by effects on gastric volumes and emptying, which may be further enhanced by foam stability. This trial was registered at clinicaltrials.gov as NCT01690182. *Am J Clin Nutr* doi: 10.3945/ajcn.114.096974

Highly Sensitive DNA Sensor Based on Upconversion Nanoparticles and Graphene Oxide

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Upconversion Nanoparticles offer a unique type of Anti-Stokes fluorescence emission under excitation with a 980 nm laser. This emission has very interesting properties due to the low background fluorescence, enormous resistance to photobleaching and no blinking effects. The rare-earth (RE) doped NaYF₄ nanoparticles present this upconversion fluorescence and present very high chemical stability. All of these characteristics make the RE-doped NaYF₄ nanoparticles (UCNPs) as interesting starting material for the development of robust and reliable sensors and biosensors.

Graphene Oxide (GO) is a 2-Dimensional material capable of quenching the upconversion fluorescence when the UCNPs are close to the surface of GO. We modified the surface of the UCNPs and functionalized with a sequence of ssDNA. The different affinity between the ssDNA and the dsDNA to the GO, attributed to the π - π interactions, permitted us to obtain a highly specific sensor with a very low detection limit.

In this work we present our results of the synthesis, surface engineering and functionalization of the UCNPs and the evaluation of the UCNPs-GO FRET pair as a sensor for a specific sequence of DNA.

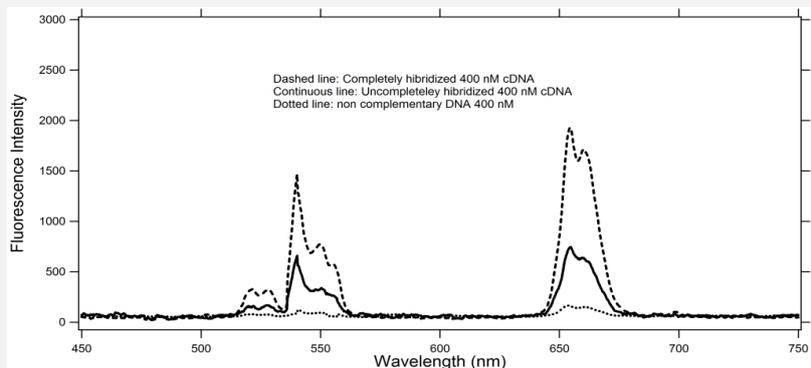


Fig. 1 Upconversion fluorescence spectra from the UCNPs-GO with hybridized complementary DNA (dashed); incompletely hybridized cDNA (continuous) and non complementary DNA (dotted).

Our study revealed a high sensitivity from the sensor to the hybridization conditions, as well as a cDNA concentration-dependant fluorescence which could be used for the quantification of the cDNA with a low detection limit.

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Coating of polymeric materials with silver nanoparticles using LbL for antimicrobial catheters

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Catheters are medical devices widely used to deliver or drain fluids from patients; unfortunately they can be colonised by microorganisms forming biofilms and causing catheter-related infections (CRIs). Silver nanoparticles are a powerful antimicrobial agent used in a growing number of products, from creams to clothes, because it is capable of inactivate resistant microorganisms and does not induce the development of further resistance among the bacteria population. Layer-by-Layer (LbL) is technique that allow the formation of coating on surfaces through a step by step deposition of molecules with opposite charges.

We prepared silicone and polyurethane (common materials used in catheters manufacturing) coated with silver nanoparticles through self-assembly of positively charged polyelectrolytes such as: Poly-diallyldimethylammonium chloride (PDADMAC) or Poly-ethylenimine (PEI) and negatively charged silver nanoparticles. The capacity of these surfaces to prevent the formation of biofilms was determined against *Escherichia coli* (*E. coli*) and *Staphylococcus epidermidis* (*S. epidermidis*). PDADMAC did not result in any visible silver coating on either silicone or polyurethane even after 5 double layers and no antimicrobial activity was detected; on the other hand, PEI produced visible coatings even after the first bilayer was applied. Visually, the deposition on polyurethane was drastically higher than on silicone. The applied silver coatings were capable of inactivating all *S. epidermidis* cells on the surface of silicone and polyurethane even with only a single polycation/silver nanoparticles bilayers. *E. coli* was inactivated only on polyurethane surfaces and not on silicone; this was a consequence of the higher resistance of *E. coli* and the lower amount of silver deposited on silicone.

Our work demonstrate the feasibility of LbL as technique to prepare antimicrobial polymeric surfaces containing silver nanoparticles; the efficacy of the coating depends on both the polyelectrolyte and the original substrate properties.

Novel graphene-polymer composite for bipolar plates, an application for fuel cells

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Synthesis and applications of graphene – polymer composites have had enormous appeal in variety of fields [1], not excluding energy related topics and areas such as fuel cells [1, 2]. As most of the efforts have been directed to improving catalyst material [3] or developing proton exchange membranes [4], other possible applications in the field, such as new graphene-polymer composite materials for bipolar plates, have not been extensively investigated [5].

In my research, I have been studying the applicability of biopolymer – graphene composite materials in fuel cells, namely as a material for electrode backing plates in fuel cell stacks. In particular, my research interests lie in the areas of interphase interactions between biopolymer and modified graphene sheets, gas and water transport mechanisms through the composite material. Biopolymers and their derivatives like chitosan based compounds [6], chitosan – alginate complexes [7], and chitosan – modified graphene composites [8] have been already tested as alternatives for Nafion© membranes, but have so far not been investigated for other possible applications in fuel cells and beyond.

In this presentation, I will report on current progress of this research.

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Conducting Polymer, Polypyrrole, Nanoparticles Modified by Proteins – Towards Biomedical Application

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Biocompatibility of conducting polymer polypyrrole [1,2] opens new directions for various biomedical applications of these nanoparticles. Therefore some advanced studies of these nanoparticles were performed. In previous our research works we have proposed enzymatic synthesis of conducting polymer layers [3] and conducting polymer based nanoparticles [4,5,6,7]. Polypyrrole [1-5,7] and polyaniline [7] based nanoparticles were synthesized by this method up to this moment.

Dynamic light scattering was applied in order to investigate changes of diameter of synthesized polypyrrole nanoparticles during polymerisation course. It was determined that during the polymerisation course the size of polymeric nanoparticles increases gradually. Evaluation of enzymatic activity of entrapped enzyme glucose oxidase (GOx) E.C. 1.1.3.4. from *Penicillium vitale* and from *Aspergillus Niger* was evaluated electrochemically and spectrophotometrically. It was demonstrated that enzymatic activity is reversibly dependent on duration of polymerisation reaction. During next stage of research the polypyrrole nanoparticles were modified by carboxylic groups and then after activation of these groups by EDC specific antibodies against selected cells were covalently attached to these polypyrrole nanoparticles. In this way modified nanoparticles were characterized. Additional biocompatibility tests in order to determine biocompatibility of polypyrrole nanoparticles with stem cells were performed.

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Solvent extraction in ionic liquids: micellization effects on extraction mechanisms

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It is now established that the mechanisms underlying solvent extraction processes are based not only on the molecular chelation properties of the extractant molecules, but also on their ability to form supra-molecular aggregates due to their amphiphilic nature [1]. A recent and promising challenge in solvent extraction is to replace the conventional organic solvents (often toxic and volatile), with ionic liquids (IL) [2]. Depending on the extraction systems tested, these new solvents show better efficiency than the conventional ones [3]. Although some assumptions based on ions exchanges have been proposed in the literature [2,3], the involved mechanisms are still poorly understood. So far, no study was conducted to evaluate the IL effect on the aggregation properties of the extractant molecules, even though ILs are known to modify the curvature radii of surfactant microemulsions [4].

Our aim is therefore to evaluate the influence of IL structure and polarity on solvent extraction mechanisms, by looking at their influence on the aggregation of the extractant molecule. We present the case of an extractant system we have already well characterized in common solvents: the HDEHP/TOPO system. The combination of these two molecules is known to allow a synergistic extraction of uranium in a ratio 4:1[5]. We showed that these synergistic properties are related to a favored aggregation [1], and combined SAXS and SANS measurements pointed out the solvent polarity influence on this system. We therefore focus here on the influence of IL structuration on extraction and aggregation properties of this system. It appears that the global uranium extraction is still efficient, but with a synergism peak, shifted to a different TOPO ratio. This interesting feature could also be related to smaller Critical aggregation concentrations.

Despite the strong structuration peaks of this kind of solvent, SAXS experiments allowed moreover observing a signal characteristic of the presence of aggregates at small angles. As the solvent peaks of IL makes a proper solvent subtraction difficult, SANS experiments were also conducted to bring a contrast complementary to SAXS measurements, and to make possible a complete analysis of the aggregates microstructure.

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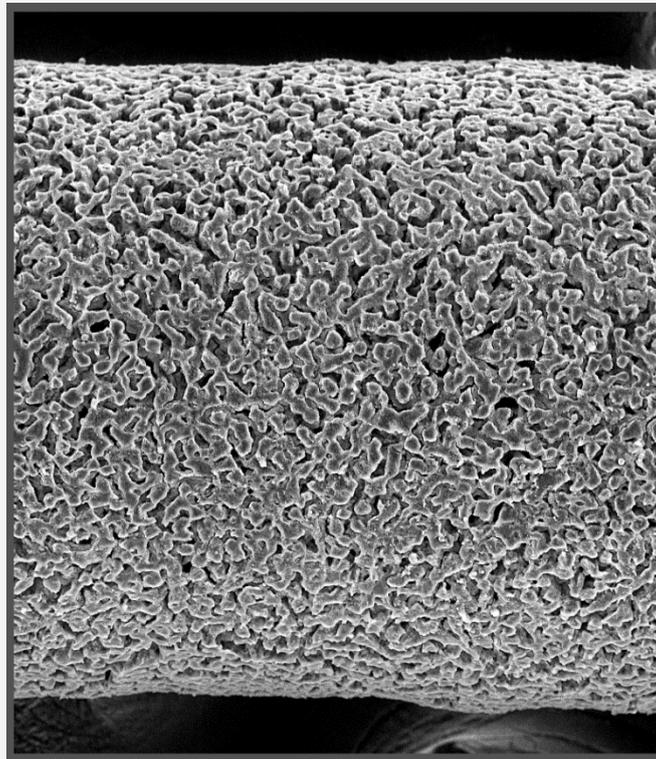
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Tailoring of Bijel fibers and membranes by mass transfer-induced liquid-liquid phase separation of ternary mixtures

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Bicontinuous interfacially jammed emulsions (Bijels) are novel soft materials with potential applications in areas ranging from healthcare, cosmetics, and food to energy and diverse chemical technologies. However, their fabrication is currently limited to only two pairs of immiscible liquids with narrow temperature windows for their formation. In such systems, typical bicontinuous domain sizes are in the range of tens of micrometers, and fabrication is inefficient due to its batch-wise nature and expensive starting materials. We explore the formation of bijels by mass transfer induced ternary liquid-liquid phase separation. The use of commercially available silica nanoparticles and ionic surfactants allows us to continuously form bijel fibers and membranes with controllable morphologies and domain sizes down to only a few hundreds of nanometers. We study the dependence of fiber morphology on different control parameters such as particle and surfactant concentration. Confocal and electron microscopy reveal hierarchical fiber architectures remarkably similar to polymer membranes formed via non-solvent induced phase inversion. However, unlike their polymeric counterparts, bijel fibers remain entirely liquid throughout their volume. This unique feature combined with the hierarchical morphology opens avenues to new applications such as bijel microfluidics or interfacial catalysis.



Complex Liquid films under MHz Substrate Vibration

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We excite complex liquid films using a MHz substrate vibration, also known as surface acoustic waves (SAWs), for studying the viscous, capillary, and convective dynamics of the films and their internal structure. Transfer of momentum from the MHz vibration in the solid substrate to a neighbouring liquid translates to a convective stress within the liquid and on its boundaries, exciting various flow patterns. The MHz substrate vibration may inflict sufficient stress on the free surface of thin liquid films to support wetting or dewetting dynamics. We study the influence of the vibration on pure liquids, solutions, suspensions, and emulsions.

In particular, we excite dynamic wetting and dewetting of evaporating complex liquids in order to study the SAW active influence on the patterns of colloidal particles deposited on the solid substrate in this process. We further examine the macroscale and microscale dynamics of thin films of emulsions and study pure liquids and surfactant solutions using microchannels and flat solid substrates. Using theory and experiment we show MHz substrate vibration changes the dynamic state of the pattern deposition of colloidal particles out of an evaporating carrier liquid, changes the internal structure of films of emulsions, and alters and support the dynamic wetting of surfactant solutions. We show the physics underlying these different systems may be explained using the convective dynamics the MHz substrate vibration excites in the liquid films.

Surfactant-free microemulsions as interfaceless dichotomic solvents

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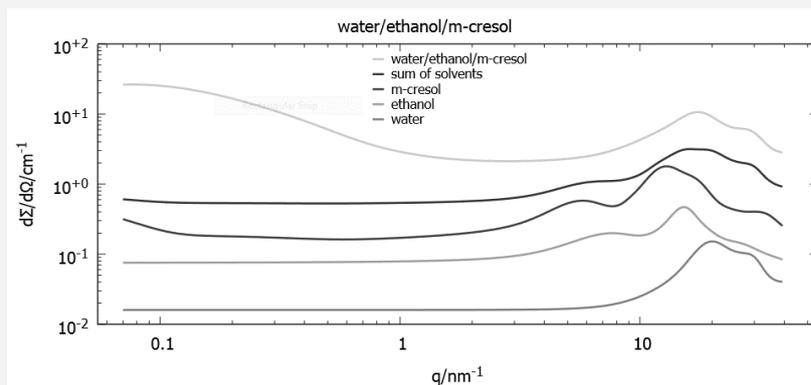
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The phase diagrams of ternary mixtures of partly miscible solvents exhibit large monophasic areas. When approaching the immiscibility gap, nm-scale fluctuations of composition are observed. This *pre-Ouzo* region corresponds to a range of composition where a micro-emulsion separates under moderate centrifugation, and shows the presence of an interfacial accumulation of the hydrotrope molecule, in most cases ethanol, that produces a labile interfacial film between oil- and water-rich domains.

We performed SWAXS (Small and Wide Angle X-ray Scattering), SANS (with contrast variation) as well as DLS and SLS to elucidate the structure of these surfactant-free micelles,[1,2] and corroborated these results with molecular dynamics.[3,4]



SWAXS spectra of, from bottom to top, water, ethanol, m-cresol, the weighted average of solvents, and the ternary mixture in the pre-Ouzo region.

A striking characteristic of these domains is the absence of a sharp interface, and correspondingly the scattering spectra are modelled by a Lorentzian profile. Pre-ouzo formulations are an excellent substrate for enzymatic reactions, separation chemistry as well as organic synthesis.

Far from being restricted to some particular ternary mixtures, we propose that these surfactant-free micro-emulsions are in fact ubiquitous, and only need a hydrotrope as cosolvent between two immiscible phases, with a quasi-equilibrium between formation of an interfacial film and water/solvent partition of the hydrotrope. We will show how hydration forces are responsible for the stability of these micelles, and the possible manipulations of their static structure and dynamics.

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Non-toxic slippery antibacterial and antibiofouling surfaces

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A simple, nontoxic and inexpensive method to prepare 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. The slippery liquid-infused porous surfaces (SLIPS) technology, inspired by the *Nepenthes* pitcher plant, was introduced by our group and provides unique capabilities that are unmatched by any other liquid-repellent surface technologies.[1] 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, brine as well as solids such as ice and wax.

Biofilms are attracting increasing attention by the scientific community due to their significant health and economic impact. We developed multifunctional coating, which will prevent the growth and proliferation of biofilms on a variety of surfaces. Our current approach is to apply a combination of nanomaterials to form multifunctional non-toxic coating that will exhibit antibacterial properties followed by surface lubrication with antibiofouling release properties. This approach was tested on various grade titanium and stainless steel surfaces and was modeled against concentrated solutions of *Staphylococcus aureus* as well as exposed the green alga *Chlamydomonas reinhardtii* culture showing excellent repellent performance.

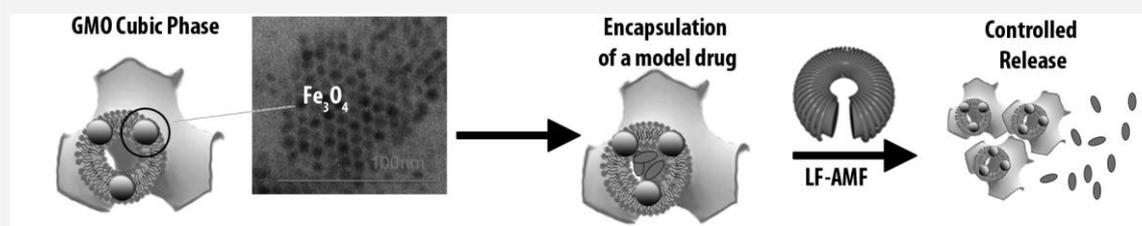
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Magnetocubosomes as responsive drug delivery systems for controlled release of therapeutics

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The design of nanostructured drug delivery systems (DDS) that improve the efficacy of therapeutic principles by enhancing their biocompatibility, bioavailability and targeting, has been the focus of extensive research over the past years. Of particular relevance in this field is the development of multifunctional architecture that can deliver different therapeutic or diagnostic agents and release them in a controlled way.



In this contribution we report on the design, preparation and characterization of a DDS where hydrophobic Fe_3O_4 magnetic nanoparticles (NPs) are included in the bilayer of bicontinuous cubic lipid nanoparticles of Glyceryl Monooleate (GMO). The “magnetocubosomes” are characterized and investigated in terms of their ability to encapsulate and release both hydrophilic and hydrophobic model drugs. Fluorescence Correlation Spectroscopy (FCS) is used to study the diffusion of encapsulated molecules inside the bicontinuous cubic phase and to monitor their release from the matrix towards the aqueous phase. In addition, we show with the same technique that magnetocubosomes are responsive to a low frequency alternating magnetic field (LF-AMF), which acts as an external trigger to boost the release of model drugs confined in the cubic phase. Magnetocubosomes represent thus a novel biocompatible, multifunctional and responsive DDS.

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Nanocubes of Prussian blue analogues: synthesis and application for the Caesium removal

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In the scope of nuclear incident on the Fukushima power plant in Japan development of new sorbents and decontamination procedures became a mission of great importance. Prussian blue and its analogues (PBA) represent a class of materials which is well established for the selective sorption of the heavy and radioactive metals such as caesium and thallium. Typical decontamination procedures involve PBA particles removal by filtration, centrifugation or magnetic separation what doesn't allow organising of a continuous process and so makes them suitable for the treatment of relatively small amount of effluent with medium to high contaminant content. In order to overcome those limitations we implement PBA nanoparticles into the flotation technique (Fig. 1). Size and surface properties of the nanoparticles along with the surfactant chemistry are main parameters determining the efficiency of decontamination process in this procedure.

Here we report the synthesis of the stable colloidal suspension of copper based Prussian blue analogue nanocubes (Cu-PBA) with the narrow size distribution and stabilized through the electrostatic repulsion. Particles size tuning was achieved by: 1) varying the speed of addition and concentration of precursor's; 2) using complexation or chelation agents for the controlled Cu^{2+} release; 3) capping of the nanoparticles with cationic polyelectrolytes. We showed also that by the flotation of Cu-PBA suspension, caesium can be efficiently removed down to the ppb level. We found that addition of non-ionic surfactant to the system reduces the particles coagulation and so increases the caesium extraction. Best results were obtained with amphiphiles possessing either ethoxy or sugar functions along with the cationic part.

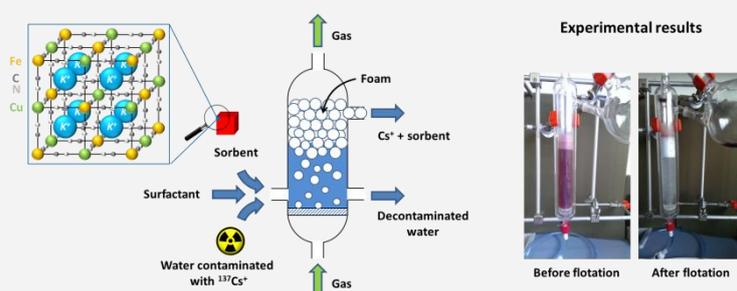


Figure 1 – Schematic representation and experimental results of decontamination process

Lung fluid : a natural protection against inhaled nanoparticles ?

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Pulmonary surfactant, the fluid lining the epithelium of the lungs, is a complex surface-active medium that contains phospholipidic vesicles and proteins. Toxicity studies have shown that inhaled nanoparticles reach the alveoli and interact with the pulmonary surfactant (Fig. 1a). As a result, the particle properties such as surface activity, stability, and cellular uptake may be modified and perturb the lung physiology.

In this work, clinically approved lung surfactant (Curosurf®, Chiesi, Italia) is investigated with different types of oxide particles (size below 100 nm), including alumina, silica, and titania. Light scattering, electrophoretic mobility, electron and optical microscopy show that vesicles and particles co-assemble into micron-sized aggregates via electrostatic interaction (Fig. 1b, c) [1]. Contrary to the models of lipoprotein corona or nanoparticle wrapping [2,3], our work indicates that the vesicles remain intact, and that particles are trapped at their surfaces. Viability assays (WST) were performed on alveolar epithelial cells (A549) using particles both with and without surfactant. In the presence of lung fluid, a net decrease of the toxicity is observed for silica particles. This result is attributed to the formation of aggregates that hampers the particle adsorption and internalization by the cells.

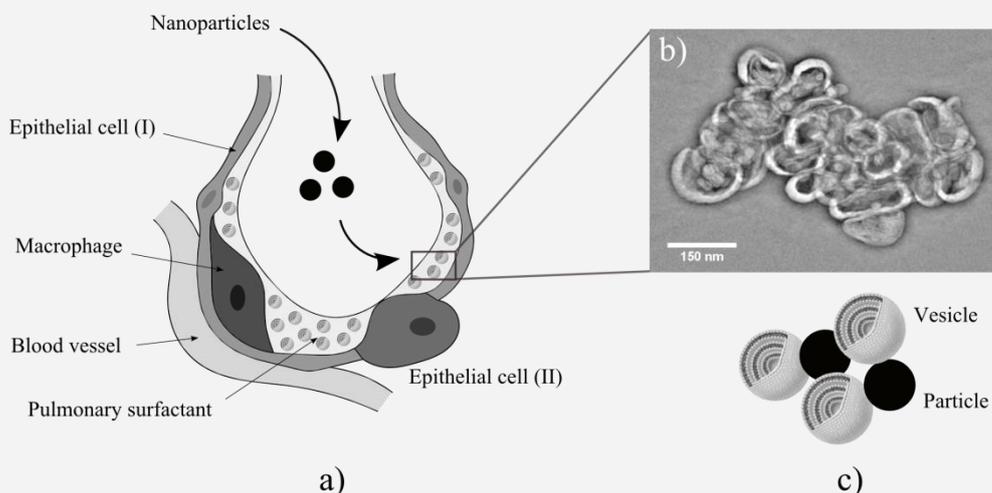


Figure 1 : a) Schematic representation of particles reaching an alveolus b) TEM picture of nanoparticles-vesicles aggregates c) cartoon of nanoparticles-vesicles aggregates

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Scaling Properties of the Shear Modulus of Polyelectrolyte Complex Coacervates: A New Time-pH-Superposition Principle

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When mixing oppositely charged polyelectrolytes under adequate conditions, polyelectrolyte complexes (PEC) can be formed. Often, synthesis of PEC leads to a phase separation either into a liquid-solid or a liquid-liquid system. The latter has a polymer-rich phase, termed coacervate phase and a more dilute phase. For studying the dynamic and structural behavior of the coacervates at different pH, rheological experiments are performed.

We investigate a system of the strong polycation poly(diallyldimethylammonium chloride) (PDADMAC) and the weak polyelectrolyte polyanion poly(acrylic acid) (PAA). The real and the imaginary part of the shear modulus (storage modulus G' and loss modulus G'') were determined in a frequency range between 10^{-3} Hz and 100 Hz at a fixed temperature of 25 °C, varying pH and salt concentration. We show that the shapes of the G' - and G'' -spectra do not change with pH-value, but that the spectra are just shifted along the axes with respect to each other. Therefore, the spectra can be superimposed to a “master curve”. Superposition principles are already a well-established tool for studying the dynamic characteristics of soft materials [1-3]. The validity of our new scaling concept implies identical mechanisms being relevant in coacervates formed at different pH, in spite of their different viscosities and degrees of dissociation on the chains of the weak polyelectrolyte PAA.

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Complete experimental equations of state of a globular protein

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Intermolecular interactions determine changes in the state of protein solutions upon concentration, such as phase transitions and aggregation. Consequently, they are determinant *e.g.* for protein function in concentrated biological media, or for protein technological use and for the performance of transformation processes. As in the general case of colloidal dispersions, changes in the state of the protein solutions are reflected by the shape of the increase of their osmotic pressure with concentration.

We established experimentally the relationship between concentration and osmotic pressure of lysozyme solutions over two concentration decades, from the dilute, “gas-phase” regime, to a concentrated, nearly incompressible, solid state, that is for protein volume fractions ranging from 0.01 to 0.63. In addition, these experimental data describe thermodynamic equilibrium states, and therefore consist in the first complete equations of state of a globular protein.

Between the dilute and the concentrated regime, we observed a transition regime where increasing concentrations result in an intermediate plateau in osmotic pressure. Small-angle X-ray scattering shows that this transition regime reflects the crystallization transition of lysozyme. In the concentrated regime, the system is fully crystallized.

In both the dilute and the transition regime, decreasing either the strength or the range of electrostatic interactions results in a shift of the equations of state towards higher protein concentrations. We describe this shift, and the overall shape of the equations of state in the dilute and transition regime, using a model with one adjustable parameter, involving a steric contribution, a short-range van der Waals attraction and a screened electrostatic repulsion.

This experimental approach, inspired of colloid sciences, can be applied to various proteins to understand the nature of their interactions and, therefore, predict and modulate their physical state upon concentration.

Hierarchical structuring of glycolipids: from simple micelles to complex biomimetic membranes

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We report structural investigation on gangliosides, biological amphiphiles typically found in the cell membranes of the nervous system of mammals. Their molecular features, a large and charged saccharidic headgroup connected to a sticky and extended ceramide double tail, strongly dictate their aggregation properties and place ganglioside aggregates at the borderline between the curved world and the flatland. All along we found the hierarchical propagation of such extreme monomer properties, from the aggregate scale to the mesoscopic phases, due to collective amplification. Surface packing optimization requires preferential mutual orientation of headgroups, giving rise to trapped solid-disordered configurations. The interplay between interparticle and intraparticle interactions gives rise to unexpected behaviours and counterintuitive phases landscape. In situ modification of monomer properties, operated by enzymatic digestion of aggregated ganglioside headgroups, either causes collective rearrangement or is overwhelmed by collective trapping, depending on their surface density. This aspect is interesting as gangliosides are not evenly distributed in cell membranes, but only in the outer leaflet, where they participate in rafts, functional microdomains enriched in special lipids including cholesterol. We recently found that ganglioside GM1 forces a preferential distribution of cholesterol, constituting a collective structural pair across the membrane. In summary, ganglioside assemblies, through cooperativity, reach a structural complexity comparable or even bigger and more adaptive than that of a protein.

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Liquid Crystals of Self-Assembled DNA Bottlebrushes

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So-called bottlebrush polymers consist of a main chain with grafted side-chains. Nature in particular exploits the extreme water-holding capacity of bottlebrush polymers with very hydrophilic side chains, in order to achieve optimal lubrication in joints and when eating food. Another use of the bottle-brush architecture in nature is to provide a hydrophilic layer that controls the spacing in bundles of protein filaments such as neurofilaments. Creating bottle-brushes with long main chains and densely packed long side chains is a challenge that has been picked up by many synthetic chemists, but typically synthetic bottlebrushes can only be prepared with relatively short main chains and side chains. We have developed diblock polypeptides with a very short cationic binding block and very long net uncharged hydrophilic block, that can coat a variety of semiflexible negatively charged polyelectrolytes (DNA) to form self-assembled bottlebrushes with extremely long main chains and very long side chains. The bottlebrush corona leads to significant main chain stiffening, and inspired by the formation of liquid crystals in biological bottlebrushes such as neurofilaments, we have started looking into liquid crystals formed by our self-assembled bottlebrushes. In this talk we will introduce the self-assembled bottlebrushes, provide evidence for the main-chain stiffening effect, and present results on the lyotropic liquid crystals that they form.
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Interactions between Charged Surfaces in the Presence of Multivalent Ions: Comparison of Counterions and Coions

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Forces between charged colloidal particles across aqueous solutions were measured with colloidal probe technique based on AFM. The interactions were measured in the presence of multivalent ions. In such experiments multivalent ions can act as counterions or coions depending on the ion charge and the surface charge of the particle. We realized both types of experiment within similar samples. The results enabled us to directly compare the effect of counterions and coions on the forces. When multivalent ions are counterions they extensively adsorb on the surface and lower its magnitude of the surface charge. This situation leads to weak and typically short-ranged forces. Interestingly, shape of the force-curve is completely changed if multivalent ions are used as coions. In such systems, forces are typically soft and long-ranged with an interesting sigmoidal shape, see Figure 1. This characteristic shape can be explained by using the Poisson-Boltzmann theory. At large distances far-field Debye-Hückel approximation can be used while at short distances near-field limit is reached. The latter represents the case where coions are completely expelled from the slit between the two surfaces.

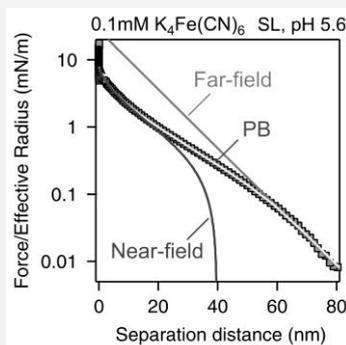


Figure 1: Experimentally measured force curve in the presence of four valent coion together with the Poisson-Boltzmann prediction and far and near-field limits.

Experimental and Theoretical Investigation on the Effect of Charge at the Interface in a Demixed Polymer–Polyelectrolyte Solution

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The interface in a demixed solution of two incompatible polymers is electrically charged when one of the polymers is neutral and the other one carries charge. The presence of the interfacial charge influences the interfacial tension and shifts the critical point of demixing. This effect of charge in aqueous two-phase systems consisting of a polyelectrolyte and a neutral polymer is investigated in experiments on mixed solutions of dextran and non-gelling gelatin, a well known food-grade model system, and using mean-field theory.

Experimentally, the interfacial electrostatic potential difference is shown to be a linear function of the difference in the concentration of charged polymer between the coexisting phases, and it can be suppressed by adding salt [1,2]; the critical demixing concentration increases with the number of charges on the polyelectrolyte [3]; the (ultralow) interfacial tension shows power-law scaling with the tie-line length, with a power of 3; and the interfacial tension drops quadratically with increasing interfacial electrostatic potential, in quantitative agreement with Poisson–Boltzmann theory [4]. It is shown that these experimental findings can all be understood on the basis of a blob model [5] extended to include the interplay of phase separation and entropy of the small ions (counterions and salt) [3].

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Assembly of Janus Gold Nanoparticles obtained via spontaneous polymer shell segregation

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Janus or double-faced nanoparticles may behave similarly to surfactants because the interparticle interactions can lead to their assembly. This behaviour can be especially important for systems formed by noble metal nanoparticles due to the possibility of controlling properties related to localized surface plasmon resonances (LSPR).

In this study, we selectively coated each hemisphere of gold nanospheres with polymers of antagonistic chemical nature creating plasmonic Janus nanoparticles. For that, we used combined two incompatible thiol-terminated polymers, polystyrene (PS) and polyethylene glycol (PEG). The one-pot coating promotes spontaneous segregation of the two polymers at nanoparticles surface.

To confirm that all nanoparticles are coated by the two polymers, the system was compared with a mixture of nanoparticles homogeneously coated by PS and PEG. When transferred to a medium, which is a non-solvent for one of the polymers (e.g. water for PS), Janus nanoparticles assemble in clusters of controlled size. In contrast, the mixture of homogeneous coated nanoparticles irreversibly precipitates.

The segregation of polymer chains was confirmed by 2D NMR. The absence of Nuclear Overhauser Effect between the signals of PEG and PS indicates that the two different polymers are not in close contact. In addition, we promoted selective growth of a silica semi-shell in the gold hemisphere coated by PEG. Due to the contrast of silica and gold, it is possible to observe the formation of Janus gold nanoparticles by TEM.

The nanoparticles assemble in different ways in solvents of different polarities and this phenomenon was investigated by UV-Vis spectroscopy and DLS. Besides, assembly properties can be controlled by changing either the molecular weight of each polymer or the nanoparticle size. The achieved control of nanoparticles assembly might be useful to tune plasmonic properties.

Effective interactions involving chemically active Janus colloids under confinement

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The area of chemically active colloids, capable of self-motility by extracting chemical free energy from their surroundings via promoting catalytically activated chemical, has received significant interest in the last decade [1,2].

Chemically active colloids, capable of self-motility via promoting catalytically activated chemical reactions in the surrounding solution [1,2], induce hydrodynamic and chemical fields that decay with the distance from the particle in a similar manner [3]. Therefore, when the active colloids are in the vicinity of walls, other particles, or fluid-fluid interfaces, a rich, complex behaviour, emerges from the interplay of the two fields (see, e.g., Refs. [4,5]).

Focusing on a simple model of diffusiophoresis of spherical active Janus colloids [3], we discuss here several examples of effects due to the spatial confinement, such as, e.g., the emergence of “hovering” states near a bounding solid surface [5] or effective attraction/repulsion to a fluid interface, for various physically plausible boundary conditions on the the particle and at the confining interface.

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Fatty acid self-assemblies in the presence of choline hydroxide: effect of the molar ratio and temperature

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Long chain fatty acids are green surfactants available in large amount in nature. To disperse them, various strategies exist such as mixtures with cationic surfactant to obtain catanionic systems or with amino counter-ions. Catanionic systems exhibit a broad polymorphism by tuning the molar ratio between the two components¹. For fatty acids combined with amino counter-ions, few data are available on the phase behavior as a function of the molar ratio¹. We investigated the effect of the molar ratio $R = n_{\text{choline hydroxide}}/n_{\text{myristic acid}}$ and the temperature on fatty acid self-assemblies in aqueous solution for choline hydroxide/myristic acid system (Figure 1)². Myristic acid ionization state was determined by coupling pH, conductivity and infra-red spectroscopy measurements. Self-assemblies were characterized by small angle neutron scattering and microscopy experiments. For $R < 1$, ionized and protonated myristic acid molecules coexisted leading to the formation of faceted self-assemblies and lamellar phases. By combining wide angle X-ray scattering and nuclear magnetic resonance, we showed that upon heating the bilayers melting process induced a structural transition from faceted or lamellar objects to spherical vesicles. For $R > 1$, myristic acid molecules were ionized and spherical micelles were present. We highlighted that R and temperature are two key parameters to tune the myristic acid self-assembly in the presence of choline hydroxide.

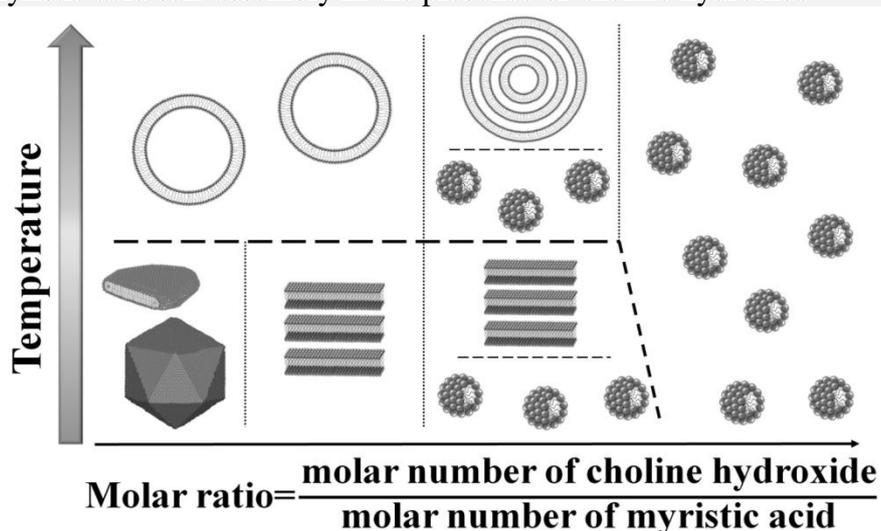


Figure 1: Phase diagram of myristic acid/choline hydroxide system

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New insights into the aggregation of surface-active substances on solids by high resolution fluorescence microscopy

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The stabilization of solid-liquid dispersions by means of additives is crucial for various applications. For a better understanding and the possibility to control the stabilizing processes, it is essential to explore the structures of surface-active substances on solid surfaces. For this aim a new approach to image these structures has been investigated using high resolution fluorescence microscopy.

Total internal reflection fluorescence (TIRF) microscopy is beneficial for imaging structures at solid-liquid-interfaces as just fluorophores at the very surface are excited. Here the environment-sensitive probe Nile Red has been used as fluorescent reporter for hydrophobic micelle cores. Since light microscopy is limited in resolution due to diffraction phenomena a post-processing of raw data can improve resolution drastically. For subdiffraction imaging the so called PAINTE (point accumulation for imaging in nanoscale topography) method was applied, which uses 2-dimensional Gaussian fitting to yield higher localization precisions. [1]

In this study, the combination of TIRF microscopy and PAINTE processing has been applied in order to image and analyze surfactant structures adsorbed onto hydrophobized glass surfaces under ambient conditions. Nonionic surfactants of different molecular weights have been compared. Micellar aggregates on surfaces were identified. The adsorption behavior was analyzed regarding shape as well as size of aggregates and the kinetics of adsorption and desorption. The surface active EO₃₇PO₅₆EO₃₇-triblock copolymer showed spherical aggregates with radii of 20-30 nm. The sizes of aggregates on the surface were compared with results from atomic force microscopy and dynamic light scattering. Regarding the adsorption and desorption kinetics, micelles of the low molecular weight surfactant C₁₂EO₆ showed shorter adsorption duration on hydrophobized glass than the high molecular weight nonionic surfactant. The importance of the structure of adsorbed layers at surfaces for various applications is discussed.

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Adsorption of phospholipids at oil/water interfaces – chemical interactions and consequences for nanoemulsions and lipoproteins

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The physical properties of adsorbed layers of phosphatidylcholines at oil/water interfaces largely differ from spread monolayers at air/water surfaces. The nature of these layers and its consequences for medical nanoemulsions, lipoproteins, and biotechnologies is however still poorly understood. Squalene or squalane as biocompatible organic phases together with phospholipids are often used to prepare emulsions for improved drug and vaccine delivery [1] but the interfacial conditions are so far not discussed intensively. We selected both oils and measured their interfacial tensions with water by profile analysis tensiometry. Equilibrium adsorption isotherms of DPPC, DMPC, and POPC, minimum molecular interfacial areas, and solubility limits were derived. These derived areas per molecule indicate that phospholipids form monolayers at the squalene/water interface, but multilayers at the squalane/water interface. The interfacial density of POPC at the squalene/water interface is much smaller than at the air/water surface because of molecular interactions. Solubility limits of different phosphatidylcholines prove that the presence of π bonds in both solvent and solute form π - π interactions that correlate with very high solubility limits as shown in squalene. However, the absence of π bonds in squalane results in extremely low solubility limits. Changes in fatty acid chain lengths show that the influence of entropy on solubility is much smaller than the π - π interactions. These findings emphasize the importance of these chemical interactions on interfacial tension and surface pressure which are of great interest for lipoproteins for instance [2,3].

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Thank you for giving the opportunity to apply for the Enzo Ferroni Award during the ECIS2015 Conference. With that abstract and further presentation I would kindly like to apply for this award.

Branched Lipids and their Interfacial Self Assembly - 3D Structures at the Water-Air Interface

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Branched fatty acids have a biological presence in hair and wool and thus form the body's outer protective layer. Nonetheless the reason for their branching - and thus their biological role/s - is poorly understood, largely due to lack of knowledge of how self assembly films respond to such targeted variations in their molecular architecture. We have brought together a thus far unique battery of techniques to address the influence of exactly such variation.

The morphology and molecular conformation of Langmuir-Blodgett deposited and floating monolayers of a selection of straight chain (eicosanoic acid, EA), iso (19-methyl eicosanoic acid, 19-MEA), and anteiso (18-methyl eicosanoic acid, 18-MEA) fatty acids have been investigated by Vibrational Sum Frequency Spectroscopy (VSFS), AFM imaging, and the Langmuir trough. While the straight chain fatty acid forms smooth, featureless, monolayers, all the branched chain fatty acids display 10 – 50 nm size domains (larger for 19-MEA than the 18-MEA) with a homogeneous size distribution. No difference between the chiral (S) form and the racemic mixture of the 18-MEA is observed with any of the utilized techniques. The aliphatic chains of the straight chain fatty acids appear to be oriented perpendicular to the sample surface, based on an orientational analysis of VSFS data and the odd / even effect. In addition, the selection of the subphase (neat water or CdCl₂ containing buffered to pH 6.0) used for the LB-deposition has a profound influence on the monolayer morphology, packing density, compressibility, and conformational order.

A measure of the hydrophobicity of films is the adsorption of surfactants to them. We find that the aggregation of surfactants on self assembly films of the branched and unbranched chains is significantly different, reflecting a different water environment. These results are discussed in terms of the monolayer structure.

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Real time monitoring of Nano Particles synthesis using in situ Dynamic Light Scattering measurements

EMRS Lille- May 2015

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Key words : Nano-particles, Dynamic light Scattering, in situ monitoring

As the number of installations of nano-particle reactors deployed in the field, either in advanced research labs or in fabrication factories, keeps growing fast, the need for reliable and accurate size monitoring tools is getting crucial. Among the important properties of nano-particles (NPs), size is probably the most critical one because it is intimately related to their physical and chemical properties like specific area/porosity, bio-availability, stability, ability to be functionalized, etc. Today, many recognized methods exist to measure the size and size distribution of nano-particles [1]. Among these methods, Dynamic Light Scattering (DLS) also known as Photon Correlation Spectroscopy (PCS) is certainly one of the prevalent techniques of choice in colloidal sciences [2, 3]; Until today, all commercial DLS setups require batch sampling which is not adapted for in situ and real time process monitoring (time consuming operation, sample stability issues, reproducibility issue, etc). Addressing this challenge implies a change of paradigm: **if you cannot bring your sample to the measurement, you have to bring the measurement to your process;**

With that idea in mind, we have developed a unique fully agile in situ DLS probe system based on an innovative approach using integrated optics and single mode optical fibers. The new probe is designed to be integrated into various environments. We present here the principle of this probe and different examples of integration in concrete applications: (i) real time monitoring and control of NPs synthesis in mili-fluidic reactor with combined and simultaneous SAXS-DLS measurement; (ii) NP synthesis kinetics monitoring into a microwave reactor; (iii) Polymer nano-emulsion control in super critical CO₂ reactor, (iv) Magnetic Hyperthermia experiments, etc.

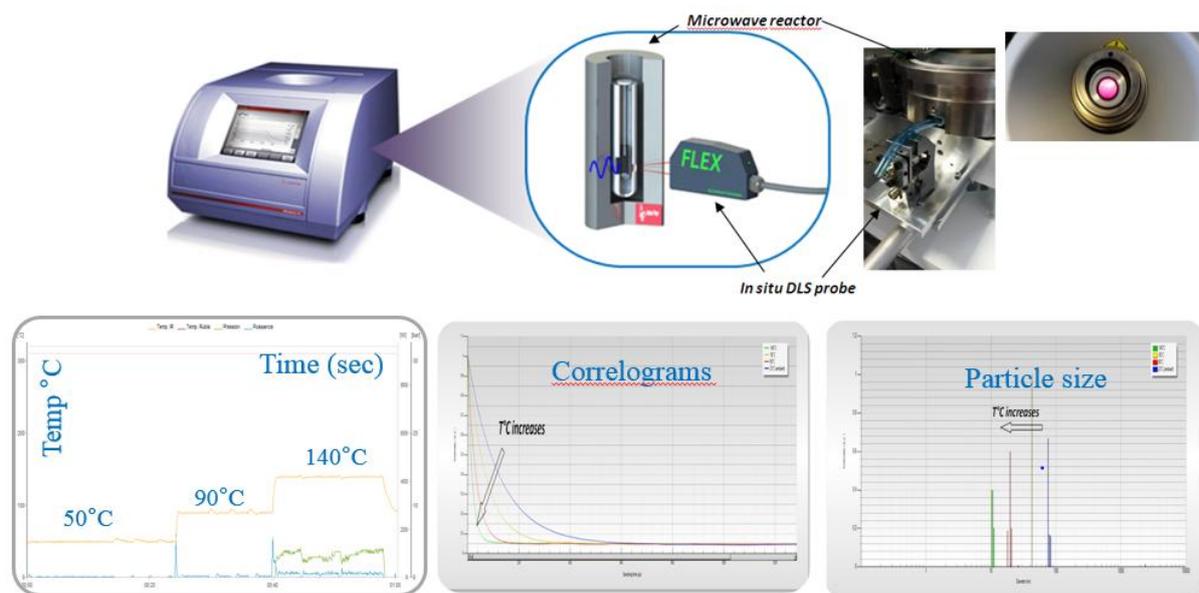


Figure 1: (up) one example of integration of the in situ DLS probe directly into a commercial microwave synthesis reactor. (Bottom): example of real time process monitoring with the in situ DLS probe.

We believe that this new remote in situ DLS system will open up new possibilities in research and industrial applications for nanoparticle characterization and fabrication.

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AM-AFM Study of the Ionic Liquid (EmIM TFSI) - Graphite Interface

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Ionic liquids are pure salts with melting points below 100 °C. Previously we have used *in situ* amplitude modulated - atomic force microscopy (AM-AFM) to resolve the structure of the ion layers in contact with the substrate at IL – mica^{1,2} and IL – graphite³ interfaces. The resolution that can be achieved with AM-AFM at *bulk* IL interfaces is similar to scanning tunnelling microscopy (STM) images of *frozen IL monolayers*. However, the capacity of AM-AFM to image bulk interfaces *in situ* with high resolution enables cause/effect relationships to be examined.

In this work we examine the effect of an applied surface potential and added electrolyte on the lateral structure of the 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EmIM TFSI) - graphite interface between ± 1 V with and without added 0.1 wt/wt% [Li]TFSI and [EmIM]Cl. At open circuit potential the interfacial nanostructure is directed by the interactions between IL ions and the surface, and with each other. Adding salt or applying a surface potential induces significant ion re-arrangements. These results significantly advance our understanding of the IL electrical double layer.

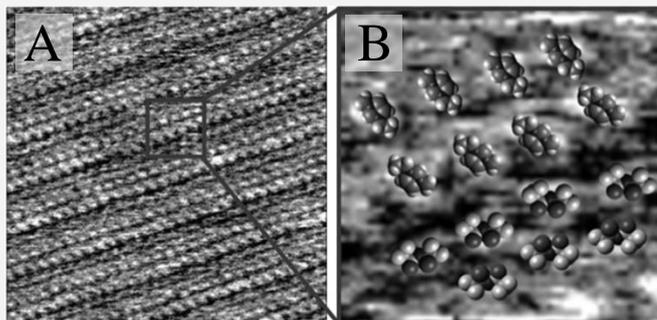


Figure 1. A) AM-AFM phase images of the EmIM TFSI - graphite interface. B) Enlarged section of image (A) bounded by the box with the postulated positions of EmIM TFSI ions.

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Cold Welding or How Soft Interactions Promote the Welding of Colloidal Gold Nanorods

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The increasing interest for the self-organization of metallic nanoparticles is due to its potential use in the construction of functional nano/micro-systems for sensing, photonics and biomolecular electronics. For these reasons, self-organization has become for the last years a major research theme in nanotechnology. One of the main factors determining the final geometry of the resulting assembly is the nanoparticle shape. At present, among anisotropic metallic nanoparticles, there is considerable interest for gold nanorods (GNR) due to their aptitude for bidirectional ordering.

Here we demonstrate a new, soft, fast and simple way to produce long gold nanowires (up to 6 μ m) based on the end-to-end self-organization and cold-nanowelding of colloidal gold nanorods in water at room temperature and without any external force. The welding of colloidal gold nanorods in water is promoted by polymer/surfactant interactions between CTAB surfactants located on the GNR surface and polymers added in solution. The GNRs self-organization process can be stopped at any time in order to control the length of the gold nanowires. The nature, functionality, concentration and the average molar mass of the polymer added in solution were investigated on the reaction rate. The kinetics of the gold nanowires formation is modelled by a oriented attachment mechanism mimicking a step-growth polymerization in which colloidal gold nanorods act as multifunctional monomer units.

This cold nanowelding technique, based on polymer/surfactants interactions, represents an attractive strategy to the bottom-up production of metallic nanowires and anticipates to be a possible future microfabrication technique with a strong analogy with polymer chemistry.

The manipulation of light using nanoscale structures is a central goal in the field of nanooptics with applications in sensing, imaging, photovoltaics and all-optical computing.¹ Due to their complex dielectric function and large permittivity noble metals are ideally suited as materials class for designing nanostructures which are capable to guide and manipulate the propagation of electromagnetic fields.² While often realized through lithographic techniques, low-cost and upscalable alternatives using colloidal building blocks gain increasing interest when it comes to the implementation into functional devices. However such a 'colloidal approach' faces many challenges like colloidal stability, colloid processing and structural control.

In this contribution we demonstrate a versatile concept for the preparation of highly ordered monolayer of hexagonally packed plasmonic nanoparticles with tunable lattice constants. This approach is based on the assembly of hydrogel-encapsulated silver nanoparticles at the water/air interface and the subsequent transfer of the monolayer onto different substrates. Due to time-dependent extension of the monolayer at the water/air interface, the dwell time for the monolayer withdrawal determines the lattice constant of the particle assembly.

We investigated the particle assemblies using imaging techniques and subsequent fast Fourier transformation (FFT). Hexagonally packed monolayer with many orders of Bragg peaks due to very high local order were found for assemblies on different substrates. The optical properties were studied by extinction spectroscopy revealing i) strongly plasmonic behavior of the monolayer, ii) homogeneous surface coverage with position independent extinction, and iii) distance dependent collective plasmonic effects.

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An anti-nematic phase of confined gold nanorods. Field-induced reorientation and optical anisotropy

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Gold nanorods have unique optical properties, which make them promising candidates for building nano-structured materials using a “bottom-up” strategy. We formulate stable bulk materials with anisotropic optical properties by inserting gold nanorods within a lyotropic lamellar mesophase: the strong confinement of the particles within the water layers induces orientational ordering of the particles, with a negative order parameter (anti-nematic phase).

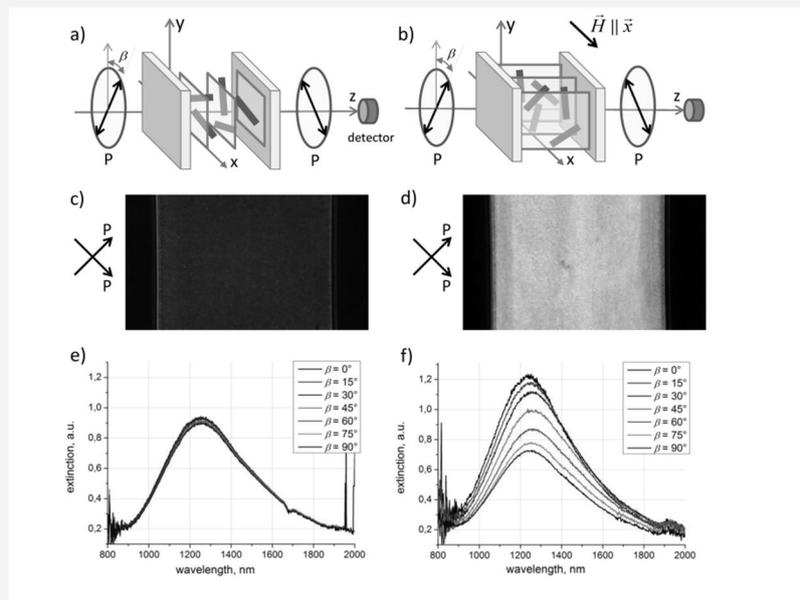


Diagram of the experimental setup, with the lamellar phase in homeotropic (a) and planar anchoring (b). The magnetic field \mathbf{H} is shown in (b). Polarized optical microscopy images for configurations (a) and (b) are shown in (c) and (d), respectively. Absorbance spectra of the longitudinal plasmon resonance peak in the infrared range for configurations (a) and (b) are shown in (e) and (f), respectively.

We also add iron oxide nanorods, which render the phase sensitive to an applied magnetic field [1]. Under field, the system switches from homeotropic to planar anchoring (see the Figure, panels a and b). In the latter configuration, it exhibits significant absorption dichroism in the infrared range, at the position of the longitudinal plasmon peak of the gold nanorods ($\lambda \approx 1200$ nm), confirming the orientation of the particles with respect to the host phase and opening the perspective of soft and addressable optical elements [2]. At the same time, the fine control over the positional and orientational order of the nanorods makes this system very promising in the fabrication of optical-range metamaterials.

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Self-assembly of Gold Nanooctahedra Supercrystals as Highly Efficient SERS-active Substrates

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In this communication, we report the size-controlled synthesis of uniform Au octahedral with well-controlled sizes and optical properties by the seed-mediated growth. Starting from single-crystalline gold nanorods as seeds, we could reproducibly obtain Au octahedra with a narrow size distribution (<7% in standard deviation) and in high purity (>95%). Moreover, the edge lengths of these Au octahedral could be readily tuned in a controllable fashion from 50 to 200 nm by varying the ratio between the seeds and the concentration of HAuCl₄ (see Figure), while keeping constant the concentration of gold salt precursor. We have investigated the specific role of butenoic acid as reducing and shape-directing agent. On the one hand, the vinyl functionality oxidizes to aldehyde while the gold precursor is reduced catalytically on the surface of the gold nanorod seeds. On the other hand, the carboxylic acid functionality stabilizes preferentially the (111) facets leading to a rod-to-octahedron transition. Once the octahedron shape is defined the shape is preserved during the growth process.

Additionally, the Surface Enhanced Raman Scattering properties of the Au octahedra were studied through the formation of supercrystals formed by densely packed nanoparticles obtained by a microfluidic-induced growth, leading to large homogenous sensing areas, and the potential to maximize the SERS signal (see Figure).

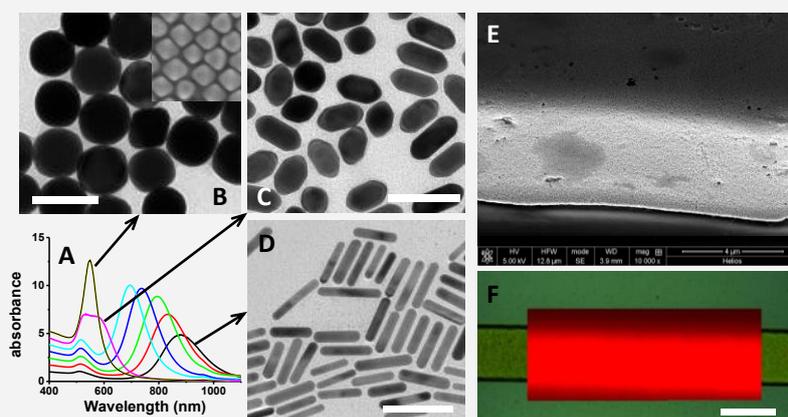


Figure. (A) Time evolution UV-Vis spectra during the gold-to-octahedron transition. Total reaction time 2 hours. (B-C) TEM images showing the particles withdrawn at different reactions time: 0 (B), 100 (C) and 120 min (D), scale bar represent 100 nm. (E) Representative SEM image showing the highly compact Au nanoparticle assembly. (F) Optical microscopy image of the microfluidic-induced assembly at which the Raman mapping was performed and the Raman intensity maps at 1371 cm⁻¹ (ring stretching, 1-naphthalene thiol), with excitation laser wavelength 785 nm.

Amino Acid-Induced Enlargement of Water Compartments in Self-Assembled Lipid-Based Nanostructures for Delivery Applications

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Self-assembled monoglyceride-based formulations show a great promise for their application as controlled delivery systems. Whereas hydrophilic substances with a low molecular weight can be incorporated in higher fractions, loading of larger molecules such as peptides and proteins is restricted due to the limited size of the water compartments.¹ The nanostructure of monoglyceride-based materials is affected by a variety of substances.^{2,3} They change the curvature of the monoglyceride layer by either bending it towards the water which leads to a shrinking of the water compartments or they can enlarge them by bending the interfacial film towards the lipophilic region. In order to serve as an additive in drug delivery formulations, those substances need to be biocompatible. Compounds that exhibit the required properties for this application are amino acids. These are a class of natural occurring, biologically important substances which are safe for being used in pharmaceutical products. The variety derives from their different side chains, which subsequently influences their impact on the monoglyceride interfacial film. Depending on the nature of the side chain, studied amino acids create the aimed enlargement of the water compartments in either bicontinuous cubic, inverse hexagonal, inverse micellar and inverse micellar cubic nanostructures.

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Strong influence of the mixing order in the complexation thermodynamics of oppositely charged PEs as probed by ITC

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Is the formulation of colloids and macromolecules that easy? Can we fully control and predict out-of-equilibrium assemblies? ¹ A central question for academic laboratories and industries where formulation is a key step; and surprisingly scarcely investigated in the literature. We have tackled this issue and recently shown the formulation pathway or the ways the various components come into intimate contact strongly influence the final morphology and properties of the complexes.² To go a step forward we have undertaken to link pathways, morphologies and thermodynamics. In this communication we show the strong influence of the addition order on the complexation thermodynamics of widespread oppositely charged polyelectrolytes comprising DextranSulfate a strong polyanion and PolyEthyleneImine a weak polycation. Isothermal Titration Calorimetry thermograms exhibit a strong dependency on the titration order with the presence of sharp peaks correlated with morphological differences. A first analysis suggests a two-step complexation process.³ Before the equivalence, the polyelectrolyte complexes (PECs) are generated through a classical ion-pairing process on both directions whereas the second step starting at the onset of the peaks is pathway-dependent. When DxS is added into PEI (I) it gives rise to an aggregation/precipitation phenomenon (liquid/solid phase transition) while the addition of PEI to DxS (II) shows a coacervation process (liquid/liquid phase transition). A sequential model was developed to account for such behavior (assembly = PECs + coacervation/aggregation) and various thermodynamics parameters were extracted suggesting an entropy driven complexation for type II experiment ($\Delta S \gg \Delta H$ et $\Delta H < 0$) through the release of counter-ions and adsorbed water while type I experiment present a overall enthalpy driven assembly leading to a denser aggregated phase ($\Delta H \gg \Delta S$ with $\Delta H < 0$). This result suggests a clear correlation between formulation pathways, final morphologies and thermodynamics and might be a useful guide to control out-of-equilibrium processes.

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Is the Hofmeister Series Exclusive to Water? Specific Ion Effects in Nonaqueous Solvents.

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Many properties of electrolyte solutions are ion specific, as they depend on the particular cations and anions present. The influence of different ions on the characteristics of their solutions usually orders according to the Hofmeister series.

Although substantial progress has been made recently, the available theories cannot yet predict how a specific ion will perturb the properties of its solution.

The achievement of a comprehensive theory of specific ion effects is of primary importance, as electrolyte solutions are ubiquitous in everyday phenomena, like the physiology of animals and plants, and in applications such as surfactants self-assembly, lipids phase behaviour and colloids flocculation.

A full understanding of salt solutions would allow us to abandon the largely empirical approach we currently employ in many scientific and technological fields, from medical science to food formulations, mineral processing and water treatment.

Our work investigates the ion-solvent interactions, and focuses on the role played by the solvent.

In order to deduce how the solvent affects the manifestation of ion specificity, we are conducting experiments in a range of polar nonaqueous liquids.

Our aim is to provide data and insights to test and expand the current theories. Here we report the results of several studies in this area.

In addition to observing how the electrostriction caused by different electrolytes changes in nonaqueous solvents with respect to water, we have recently conducted Size Exclusion Chromatography (SEC) of several salts in nonaqueous solvents, and we have studied the influence of electrolytes on the swelling of polymeric brushes by Quartz Crystal Microbalance (QCM).

Our results contribute to the present understanding and provide significant proving ground for theories of specific ion effects.

Tailoring the phase structure from lipase-responsive phytantriol-based nanoparticles stabilized by polysorbate 80

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Lyotropic liquid crystals are attracting increasing attention as drug release devices due to their unique physicochemical properties and tunable phase structure, which can influence the drug release kinetics [1]. Controlling the phase structure of dispersed lyotropic liquid crystals using enzymes as triggers is an exciting and emerging area. In this work we propose to use lipases to triggering phase transitions of phytantriol-based nanoparticles at the same time that the liquid-crystalline lipid is not completely degraded by the hydrolytic reaction. This is advantageous because the drug should not be released prematurely due to nanoparticle disintegration, which could impair the effectiveness of drug targeting in vivo. The liquid-crystalline nanoparticles were prepared by a solvent displacement method [2]. The cleavable cationic surfactant decyl betainate chloride was added as minor component and the nanoparticles were stabilized by polysorbate 80. The nanoparticles showed low polydispersity and mean sizes around 200 nm by dynamic light scattering. The analysis by small-angle X-ray scattering (SAXS) technique (D11A-SAXS1, LNLS – Campinas/Brazil and I911-SAXS, MAX IV – Lund, Sweden) evidenced a cubic phase with space group Q229 (Im3m). Time evolution of the phase structure in the presence of lipases was followed at every 10 min by SAXS to identify transitions induced by these enzymes. Interestingly, phase transitions were not triggered by lipases without the presence of the cationic surfactant despite the ester bonds from polysorbate 80. On the other hand, a phase transition from cubic to reverse hexagonal phase was observed in samples containing decyl betainate chloride as minor component. The results suggested that interaction between the phytantriol-based nanoparticles and lipases was tuned by differences on the nanoparticle interface promoted by the cleavable surfactant.

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On the release of cargo molecule from a poly(N-isopropylacrylamide) brush

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The controlled release of cargo molecules by a polymer film has potential to deliver the required components in lubrication, anti-fouling, drug-delivery and other clean tech applications. The aim of this work is to monitor the release of cargo molecules by change in temperature, pH or ionic strength. The thermoresponsive polymer, poly(N-isopropylacrylamide) (pNIPAm) was chosen as an example system as its bulk properties in aqueous solution are well known. Its conformation at the surface is, however, less well understood. pNIPAm films are grown on a solid (fused silica) substrate, and atom-transfer radical-polymerization (ATRP) protocols[1] have been explored to vary the film density. Phase transitions are monitored in situ by a surface-selective technique, total internal reflection (TIR) Raman spectroscopy. The uptake and release of a cargo molecule has also been investigated using TIR Raman. Changes in molecular interactions and orientations were recorded with 1 second time resolution. The methods are not limited to pNIPAm and could be used for studying the interaction between a block copolymer and a cargo.

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Thermosensitive Nanogels at the Air/Water Interface - a Neutron Reflectivity Study

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Thermosensitive nanogels (swollen colloidal particles consisting of cross-linked polymers) show great promise as intelligent materials for biomedical applications, cosmetics, separation techniques and as a key constituent of model colloids. Recently poly(*N*-isopropylacrylamide), pNIPAM, based gel particles have emerged as a new tool to stabilize interfaces in Pickering emulsions and foams. The swollen polymeric character of the gels facilitates their transport from solution to fluid interfaces where they undergo substantial deformation. Understanding the adsorption dynamics of those nanogels and the mechanisms that allow them to stabilize the interfaces are the important issues that need addressing to achieve tailored particles.

The main objectives of this study were to use neutron reflectometry (NR) to probe the interfacial properties of pNIPAM nanogels and to examine how the related interfacial structure varies with the temperature at the air/water interface. In the present work series of pNIPAM nanogels with different amount of cross-linker (*N,N'*-methylenebisacrylamide, MBA) and appropriate deuteration labelling have been prepared and characterized (size, polarity, and ability to lower water surface tension). NR technique was used to quantify the nanogels adsorbed at the air/water interface and to study their conformational changes as a result of variations in temperature. The data obtained contribute to the understanding of how these particles stabilize the interface, which are the factors influencing their adsorption and to establishing a relationship between their molecular structures and behaviour at interface.

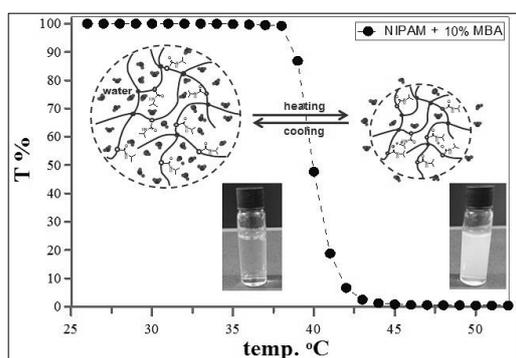


Fig. 1. Transmittance (T%) of pNIPAM nanogels cross-linked with 10% of MBA as a function of temperature.

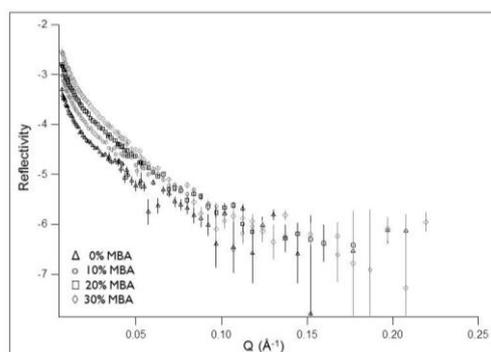


Fig. 2. Reflectivity profiles for a series of pNIPAM nanogels cross-linked with different amounts of MBA at the air/water interface.

Amphoteric Core-Shell Microgels and their Interaction with Polyelectrolytes

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Amphoteric microgels are soft, cross-linked polymer networks which contain both cationic and anionic co-monomers. The acidic or basic groups become ionized with change in pH and thermosensitivity is induced using *N*-isopropylacrylamide (NIPAM) as a building block. A core-shell morphology with a heterogeneous charge distribution is obtained by a two-step seed-and-feed polymerization. As soon as charged moieties are present in the polymer network, they attract counterions because charge compensation is required due to electroneutrality. At low and high pH, the presence of counterions promotes swelling of the microgel. In the intermediate region positive and negative charges become equal and charge compensation by counterions is no longer necessary. The release of these counterions results in a decrease of the osmotic pressure and a shrinkage of the microgel size. The electrostatic attraction between opposite charges causes the microgel to shrink more as compared to a neutral one. We studied the volume transitions of amphoteric core-shell microgels as a function of pH with small angle x-ray scattering (SAXS) and compared our results with molecular dynamics simulations of a single amphoteric microgel within a coarse-grained model and implicit solvent. Furthermore we studied the uptake and release of guest polyelectrolytes oppositely charged to the microgel core, but with the same sign of charge as the microgel shell. In amphoteric systems, multiple interactions act simultaneously or compete against each other within the microgel interior. With a combination of scattering techniques and simulation methods, we investigated how these interactions are affected by its environment like pH, ionic strength and quality of the solvent.

Field-induced Assembly of Superparamagnetic Colloidal Spheres Confined in Thermo-reversible Microtubes

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Molecular microtubes self-assemble from an aqueous solution of sodium dodecyl sulfate and cyclodextrin. These microtubes may incorporate non-magnetic colloids with anisotropic shapes and various materials to form ordered 1D structures.[1-2] Structural transformations of superparamagnetic colloids confined within these self-assembled microtubes are studied by systematically varying tube-colloid size ratios and external magnetic field directions in this work. A magnetic field parallel to microtubes may stretch non-linear chains like zigzag chains into linear chains. Non-parallel fields induce new structures including kinked chains and repulsive dimers that are not observed for unconfined magnetic colloids in bulk. Model calculations further confirm that tube-colloid size ratio significantly influences the magnetic response of confined colloids. All observed field-induced transformations in microtubes are reversible provided the microtubes are not completely filled with colloids. We also extend one microtube subsystem to multiple well-aligned microtubes system to achieve magnetic responsive 2D crystallization. On application of a magnetic field before tube formation, the assembly of superparamagnetic colloidal chains into the microtubes was examined at single particle level.

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Spatial and Orientational Control on Anisotropic Colloids by Electric and Magnetic Fields

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Living organisms combine soft and hard components to fabricate composite materials with out-standing mechanical properties^[1]. The optimum design and assembly of the anisotropic components reinforce the material in specific directions against multidirectional external loads^[2]. Although nature does it quite readily, it is still a challenge for material scientists to control the orientation and position of the colloidal components in a matrix. Here, we use external electric and magnetic fields to achieve positional^[3] and orientational^[4] control over colloid-polymer composites to fabricate mechanically robust materials to capture some of the essential features of natural systems. We first investigated the assembly of spherical micron-sized colloids using dielectrophoresis, as these particles provided an easily-accessible and instructive length scale for performing initial experiments (Figure). We used dielectrophoresis for spatial control of reinforcing anisotropic components and magnetic fields to provide control over the orientation of the reinforcing constituents.

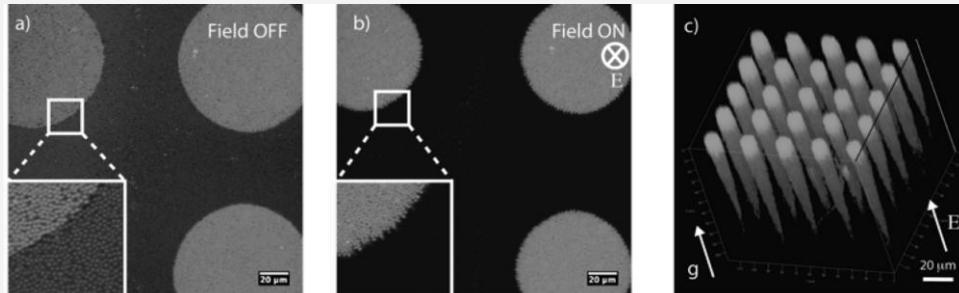


Figure | Directed self-assembly of fluorescently labelled spherical colloids. Fluorescent colloids were spread all over the sample cell one minute after the field is turned off. Inset is the edge of the well (a), when an electric field of $1V_{\text{rms}}/\square\text{m}$ is applied particles move towards low-field regions (to the holes of the electrode)(b). The assembly spans the volume between the two electrodes and forms a 3D pillar that is getting thinner towards the unpatterned electrode. The aspect ratio of the pillar is approximately 10, where the height is $100\ \mu\text{m}$ and diameter is $10\ \mu\text{m}$ (c).

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Supraparticles from emulsion-assisted self-assembly: formation and stability for different core materials, ligands, and surfactants

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Supraparticles are regular arrangements that contain defined numbers of colloidal particles. Here, we discuss supraparticles that form from nanoparticles in emulsions. Monodisperse, sterically stabilized nanoparticles (NP) were confined inside the dispersed nonpolar phase of an oil-in-water emulsion. Upon evaporation of the oil phase, the NP concentration increased and the particles arranged into supraparticles [1]. Structure, stability and formation of the supraparticles depended on the NP core material, ligand, surfactant, and on process conditions like temperature. We studied the structure and shape of supraparticles formed under different conditions with dynamic light scattering, small angle X-ray scattering and transmission electron microscopy. We find that alkanethiol-stabilized gold or silver NP with core radii between 2 and 4 nm arrange into regular supraparticles if the temperature is above a critical temperature and a surfactant blocks the liquid-liquid interface [2]. Alkanethiol-capped cadmium selenide quantum dots did not assemble into ordered supraparticles under any condition that we tested, perhaps due to their lower Hamaker constant. Oleylamine-stabilized gold NP formed supraparticles, but the NPs coalesced after a few weeks and the supraparticles were transformed to metal spheres (Figure 1). We attribute this ligand effect to the lower gold affinity of oleylamine compared to alkanethiols.

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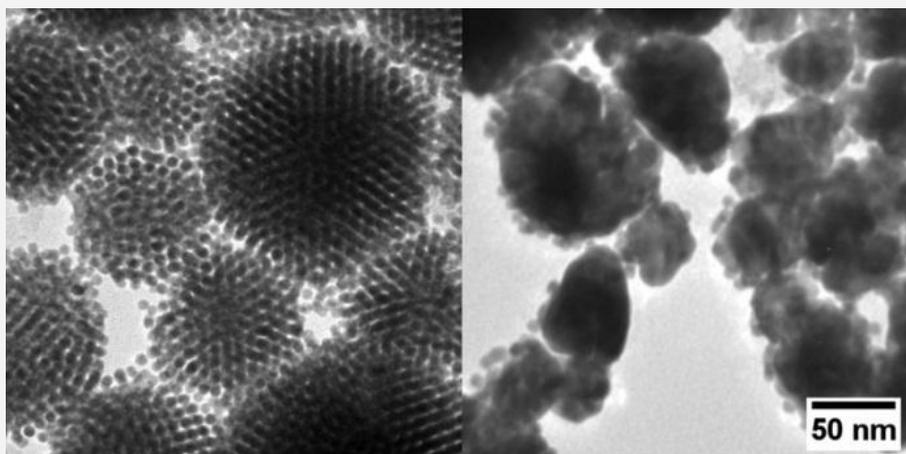


Figure 1: Supraparticles composed of oleylamine-stabilized gold nanoparticles directly after formation (left) and after one month (right).

First observation of Laves phases in binary hard sphere colloidal mixtures

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Polystyrene (PS) microgel colloids serve as model system for hard spheres (HS). Binary mixtures of dispersed small (S) and large (L) PS particles with diameter ratios of S to L close to $\Gamma=0.8$ have been widely used to investigate glass formation as well as re-entrant melting introduced by short-ranged depletion attraction.

Previously, we have shown that depletion attractions not only enhance particle mobility, leading to a melting of the glass, but also enforce crystallization of a binary mixture. Whereas such colloidal alloy formation was found to be kinetically suppressed in purely hard sphere mixtures [1], crystallization could be enforced at a volume fraction slightly below the glass transition upon introduction of attractive forces [2]. Surprisingly, recent investigation of a similar but purely repulsive binary PS microgel system with a slightly different Γ revealed crystallization near the glass transition volume fraction. Using static light scattering to investigate the structure of the sample, we observe hexagonal superlattices instead of single-component fcc crystals.

Our findings can be rationalized by the occurrence of stable binary crystals LS_2 , so-called Laves phases, with the crystal structure being astonishingly identical to that found in $MgZn_2$ alloys. Laves phases are discussed as precursors for the preparation of photonic band gap materials [3]. They have been predicted in computer simulations by Hynninen et al. [4], but have so far not been experimentally observed in hard sphere-like polymer colloids.

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Experimentally disentangling the glass and the jamming transition in charge stabilized nanoemulsions

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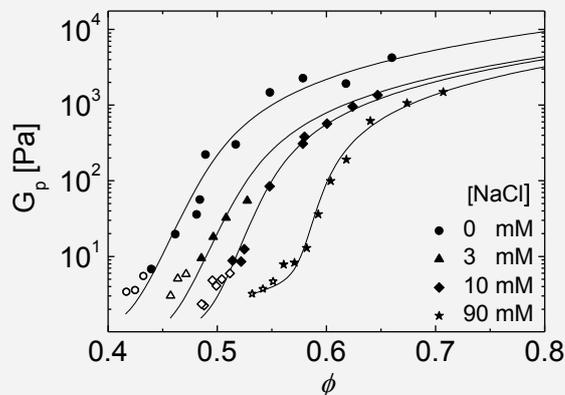
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We discuss dynamic properties of concentrated silicone oil-in-water emulsions, amorphous disordered solids composed of repulsive and deformable soft colloidal spheres [1]. For emulsions of nanoscale droplets, known as nanoemulsions, the radius begins to approach the Debye screening length. Such charge-stabilized nanoemulsions can become elastic solids at very low droplet volume fractions [1]. Using dynamic light scattering and diffusing wave spectroscopy we continuously monitor the internal dynamics while increasing the droplet concentration in small steps. The mean size of the particle has been chosen to be $d = 250\text{nm}$ such that at the inverse scattering wave number $2\pi/q$ we probe the dynamics at typical inter-particle distances. Changing the electrolyte concentration we can control the effective stiffness of the interaction potential which then allows the decoupling of the glass and the jamming regimes. As shown in the Figure below the estimate of the elastic modulus G_p derived from light scattering as a function of volume fraction exhibits a transition from a soft to a hard solid for all samples. The nature of the transition however changes significantly upon increasing the electrolyte concentration (from 0mM to 90mM). For low salt concentrations interactions are soft and long-range and the transition is smooth; the glass and the jamming regimes are basically indistinguishable. However, at high enough salt concentrations (90mM) the interactions are stiffer and we can clearly identify an entropically dominated regime at low volume fractions decoupled from the jamming transition at higher concentrations. For the latter the elasticity is set by surface tension upon deforming the droplet interfaces [2].

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Elastic modulus of dense emulsions for different electrolyte concentrations, droplet diameter $d=250\text{nm}$.

Dendrimer nanofluids in the concentrated regime: From polymer melts to soft spheres

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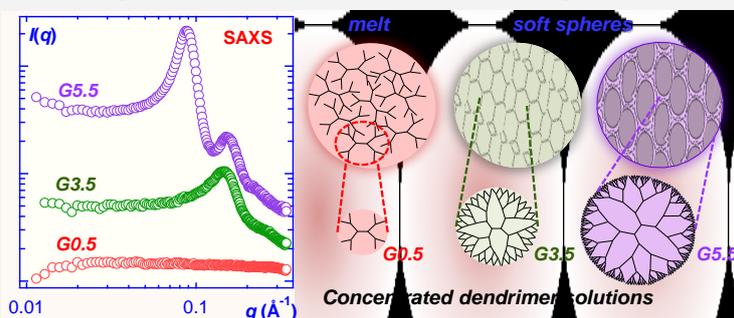
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Understanding dendrimer structures and their interactions in concentrated solutions is important to a wide range of applications, such as drug delivery and lubrication. However, controversy has persisted concerning whether, when confined to proximity, dendrimers would entangle as observed for polymer systems, or act as deformable spheres. Furthermore, how such behaviour may be related to their size-dependent molecular architecture remains unclear.

Using small angle X-ray scattering (SAXS), the intermolecular interactions and structures in aqueous nanofluids containing three generations of carboxyl terminated poly(amidoamine) (PAMAM) dendrimers (G0.5, $R_g = 9.3 \text{ \AA}$; G3.5, $R_g = 22.6 \text{ \AA}$; G5.5, $R_g = 39.9 \text{ \AA}$, where R_g is the radius of gyration) over a mass fraction range $0.005 \leq x \leq 0.316$ have been studied. In the highly concentrated regime ($x \geq 0.157$), we observe that the solution properties depend on the dendrimer generation. Our results suggest that the smaller G0.5 dendrimers form a highly entangled

polymer melt, whilst the larger dendrimers, G3.5 and G5.5 form densely packed and ordered structures, in which the individual dendrimers exhibit some degree of mutual overlap or deformation. Our results demonstrate the tunability of inter-dendrimer interactions *via* their molecular architecture, which in turn may be harnessed to control and tailor the physical properties of dendrimer nanofluids.



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Three-dimensional nanoscopy of thermosensitive Poly(N-isopropylacrylamide) microgel particles

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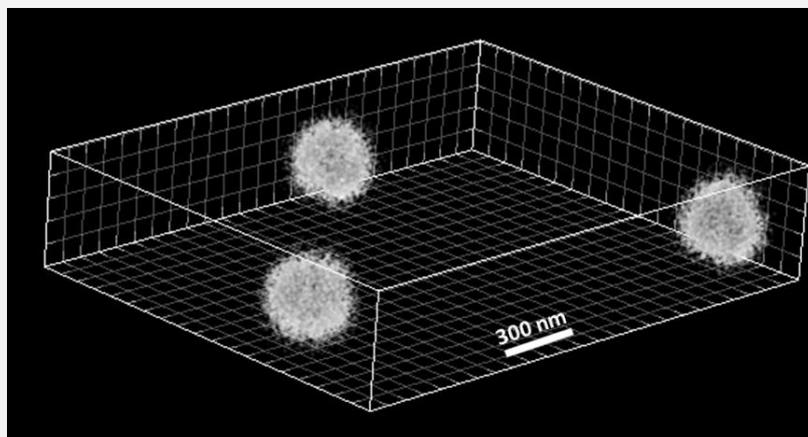
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Polymers structures such as PNiPAM microgels have been extensively studied for their ability to undergo significant structural and physical transformations that can be controlled by external stimuli such as temperature or pH. Despite this plethora of published work many fundamental questions remain unresolved. The mechanism that leads to the volume phase transition of PNiPAM microgels for example is not well understood and its consequences towards the microgel architecture on nanoscopic length scales are unclear. It is still a puzzle, for example, that even in the collapsed state microgel particles contain a substantial amount of water. Moreover the transition between swollen and collapsed microgels is less abrupt than expected for a phase transition and shows hysteresis. However it is unclear to what extent these observations can be associated to individual particle properties or whether polydispersity in the ensemble of microgel particles is responsible. Scattering techniques are not well apt to answer any of these questions since they only provide access to ensemble averaged structural information in reciprocal space. Single particle observations in situ have so far been hindered by insufficient resolution, with optical microscopy, or contrast, with cryo-TEM. However, in recent years super resolution microscopy techniques have emerged that in principle can provide nanoscopic optical resolution.

Here we report on the in-situ three-dimensional nanoscopy of dye-labeled submicron sized PNiPAM microgels during a temperature scan revealing the internal microstructure during swelling and collapse of individual particles [1]. Using direct Stochastic Optical Reconstruction Microscopy (dSTORM) we demonstrate a lateral optical resolution of 30nm and an axial resolution of 60nm. We present results on the internal density distribution in the swollen and collapsed state and the particle-to-particle variability of the volume phase transition.

[1] G. M. Conley, S. Nöjd, M. Braibanti, P. Schurtenberger, and F. Scheffold, in preparation.



Temperature-Induced Packaging of Ferricyanide by Help of Cationic Microgels

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Microgels are spherical and soft polymeric particles consisting of a crosslinked and porous network with unique properties. The huge scientific research interest in these “smart” polymers is illustrating their wide field of potential applications due to their stimulus responsiveness and the ability to undergo a volume phase transition with respect to environmental changes.

Furthermore polyelectrolytes interact strongly with multiple-charged counterions leading to a host-guest interplay in case of charged microgel networks. The charge of guest molecules (e.g. inorganic coordination compounds) can be changed by various means. Besides light-sensitive counterions,^[1] electrochemically-addressable counterions are of scientific interest since years. For example, electrolysis of complexes between linear polyelectrolytes and hexacyanoferrates lead to film formation onto electrodes,^[2] while the charge transport through the films is still facile.^[3] At the same time, the polymer architecture has an influence on these processes. We could show recently that the use of branched bis-hydrophilic polymer structures together with the mobility of the redox-active species favours bulk aggregation instead of film formation on the electrode.^[4] Simultaneously, the electrochemical switching of macromolecules between the unimeric and the micellar/vesicular state could be observed for the first time. We now address thermoresponsive cationic microgels and their influence on the electrochemistry of hexacyanoferrates. The combination of hydrodynamic voltammetry and electrochemical impedance spectroscopy methods allowed a distinction between the electron pathways. In addition, the data strongly suggest the selective uptake of ferricyanide and an encapsulation of the guest molecules inside the microgel network at elevated temperatures. Furthermore the temperature-induced microgel collapse leads even to an increased uptake and hence to a decreased electrochemical accessibility of the entrapped counterions in the heat. In addition the size of the cationic microgel can be manipulated by electrochemical switching leading to novel multiple stimuli - temperature and redox - responsive microgels, with a preferential interaction of the less charged ferricyanide counterion.

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Doubly Crosslinked Poly(*N*-Isopropylacrylamide) Based Microgel Prepared by Host/Guest Interactions

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Doubly crosslinked microgels are new type of hydrogels, which are formed by crosslinking of microgel particles ($d=100-1000$ nm) prepared previously. When poly-*N*-isopropylacrylamide (pNIPAm) microgels are cross-linked to form a macroscopic gel network, their thermoresponsive properties are maintained but the formed macroscopic gel network can exhibit much faster swelling kinetics than traditional hydrogels. There are few ways to produce such systems, but most of them based on the formation of permanent covalent bonds among the gel particles. However, recent computational models indicate that the presence of labile bonds among the gel particles can lead to unique self-healing and mechanical properties.

Here, we report the preparation of doubly crosslinked microgels by utilizing host/guest interaction for crosslinking the microgel particles. We investigated two alternative approaches to obtain a macroscopic gel network. In the first case a pNIPAm core / 100%AAc shell microgel and a cationic poly(β -cyclodextrin) (pCD) polymer were used to form a pCD shell on the microgel particles. In the second case the β -cyclodextrin shell of the pNIPAm microgel particles was established by copolymerizing β -CD-functionalized co-monomers into the outer shell of the microgels. The CD functionalized microgels were crosslinked by adamantane-grafted dextran to give rise to the macroscopic gel network.

The resulting doubly crosslinked gels are stable and their rheological properties were studied by dynamic rheology measurements. The effect of temperature, ionic strength and composition was investigated on gel formation. It is concluded that host/guest interaction can be successfully applied to form a unique class of doubly crosslinked microgel networks that are promising candidates e.g as injectable responsive gels or as a biocompatible scaffold.

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Unconventional Critical Behavior in Poly(*N*-isopropylacrylamide) Microgels as Revealed by Simultaneous Small- and Wide-angle X-ray Scattering

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When temperature is raised, poly(*N*-isopropylacrylamide) (pNIPAm) exhibits a coil-to-globule transition at a critical temperature, $T_C \approx 32$ °C, in aqueous media [1]. Correspondingly, pNIPAm-based hydrogels show a volume phase transition (VPT) near T_C , being swollen and deswollen below and above T_C , respectively [1]. Such phenomena essentially come from a balance between hydration of an amide group and hydrophobic interaction between isopropyl groups. It has been shown that pNIPAm-based bulk gels involving a macroporous gel (cryogel) belong to the Ising universality class, as they exhibit critical behavior well described by 3D-Ising model [1,2]. However, there has still been a controversy on the critical behavior of the so-called microgels [3,4].

In this contribution, we discuss temperature-dependent internal structures of submicron-sized thermoresponsive microgels and their critical behavior by means of dynamic light scattering (DLS) and simultaneous small- and wide-angle X-ray scattering (SWAXS) experiments covering $0.05 \leq q/\text{nm}^{-1} \leq 25$. A series of pNIPAm-based microgel samples having different crosslink densities and particle diameters were prepared via aqueous free-radical precipitation polymerization using a water-soluble anionic initiator KPS, in which *N,N'*-methylenebis(acrylamide) (BIS) was used as a crosslinking agent.

All microgels dispersed in water exhibited simultaneous divergence of the correlation length, corresponding to the length scale of the density fluctuation caused by the polymer network, and the asymptotic Ornstein-Zernike forward intensity, being inversely proportional to the osmotic compressibility. The observation demonstrates the separation into nano-sized water-rich and polymer-rich domains toward T_C . Furthermore, we found that the VPT of the present microgels is not perfectly consistent with widely known universality classes.

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Insights into particle nucleation mechanism and late reaction multiplet formation in precipitation polymerization of N-isopropylacrylamide

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Poly(N-isopropylacrylamide microgels) are spherical stimuli-sensitive polymer particles in the diameter range of fifty nanometers to one micron. They are conveniently prepared by precipitation polymerization in water and form colloidal particles with narrow size distribution. However, the mechanism of particle formation is not thoroughly understood, which poses a challenge to microgel particle size customization for the many applications of these particles.

We have previously shown by 3D-DLS measurements that polymerization rate in this reaction is independent of particle number in the batch and that the reaction proceeds initially as solution polymerization [1]. Our new results show that the particle number in the batch, and thus the final particle volume, is consistent with the kinetic chain length predicted by the solution polymerization kinetics. We apply this new insight in chain transfer modulated charge exclusion synthesis, which drastically increases final particle volume of the polymer particles.

Furthermore, we report that under suitable polymerization conditions microgel particles can be made to aggregate to form doublets, triplets and higher order aggregates (**Fig. 1 A**). We use microgel aggregation scattering model to estimate the fractions of each species from static light scattering data (**Fig.1 B**) in order to investigate to which extent the aggregation can be controlled by reaction conditions.

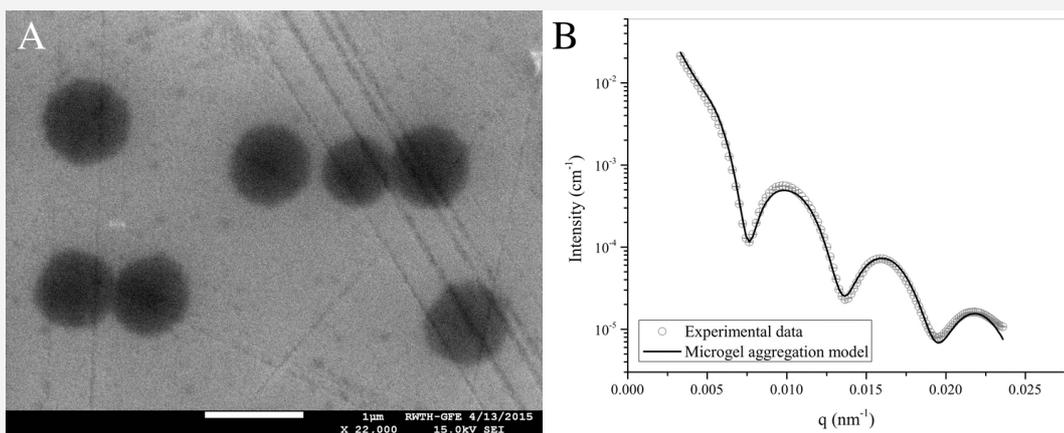


Figure 1. A: Scanning electron micrograph of singlets and microgel dumbbells formed in batch synthesis **B:** Static light scattering measurement of a batch containing singlets, dumbbells and triplets fitted with microgel aggregation model.

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Multipolar Attraction of Colloidal Nanocrystals in Apolar Solvent

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While much effort is devoted to develop colloidal particles with chemically different surface patches, we conclude from the interactions of apparently homogeneous nanocrystals in apolar solvents that they are inherently patchy on the atomic scale. Quantitative information about the interactions of sterically stabilized PbSe quantum dots was obtained from various techniques: cryogenic electron microscopy,[1-4] small angle X-ray scattering,[1] analytical centrifugation,[1] and dielectric spectroscopy.[5] The attraction between the particles is too strong to be explained by Van der Waals interactions, and the permanent electric dipole moment is not high enough either. As the particles have no net charge and attraction is found to scale with the surface area of the particles, our explanation is multipolar interactions, with on each particle the same number of positive and negative surface sites. This hypothesis was tested by numerical calculations of the interaction of sterically stabilized spheres with randomly positioned surface charges.

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Directing colloidal self-assembly using supramolecular chemistry

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The control over the colloidal interactions is highly important in view of the high number of applications where colloidal-based materials are used. This can be addressed by decorating colloids with supramolecular colloids, whose interactions are strong, directional and temperature-reversible in solution [1]. While literature on supramolecular polymers is extensive, little is known about their impact on colloids [2]. In our approach the supramolecular moiety used is a benzene-1,3,5-tricarboxamide (BTAs) derivative. Such BTA molecule recognizes and selectively interacts with identical BTA through a 3-fold intermolecular hydrogen bond. The BTA is also equipped with a photo-cleavable group, which blocks the formation of the hydrogen-bonds when present. All these features allow tuning the self-assembly of the colloids by using two different external triggers: UV-light and temperature. The synthesized supramolecular colloids were characterized by several techniques and their self-assembly upon UV irradiation was followed by means of confocal microscopy. Our studies revealed that particles remain as singlets as long as the protecting group is present. The cleavage of this protecting group by light activated the short-range hydrogen-bonding interactions of the supramolecular moieties, which in turn triggered the colloidal clustering. The obtained results clearly evidenced that the clustering of the colloids at the macroscopic level was a direct consequence of the intermolecular hydrogen bonds at the molecular level. The effect of the amount of active sites on the binding strength as well as the self-sorting capacity (orthogonality) were explored. The behaviour of these supramolecular colloids demonstrates that small surface-grafted molecules can have a dramatic effect on the behaviour of colloidal particles. These findings pave the way to create new complex colloidal materials.

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Depletion Controlled Surface Deposition of Uncharged Colloidal Hard Spheres from Stable Bulk Dispersions

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We have studied experimentally the competition between adsorption of particles to a flat surface and bulk aggregation of particles, when the particles and substrates are of the same material, for hydrophobic silica spheres dispersed in cyclohexane in contact with hydrophobic silica surfaces. The effect of increasing the depletion attraction between the hard-sphere-like particles in the presence of a surface by increasing the concentration of the depletant, poly(dimethyl)siloxane, was investigated.

Adsorption from particle dispersion, as observed by ellipsometry, was found to occur as the attractive interaction between the particles was increased. Surface adsorption occurred at depletant concentrations far below those required for bulk aggregation. Turbidity and viscosity measurements confirmed that no bulk aggregation occurred in the window of the interaction strength where surface adsorption occurred.

The obtained results agree well with previously published theory and simulations predicting that surface adsorption should precede bulk aggregation solely due to geometrical effects [1].

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Shape-controlled Nanoparticle Assembly Mediated By Electrostatic Complexation With Long Polyelectrolyte Chains

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The complexation of long polyelectrolyte chains with oppositely charged nanoparticles (NPs) could lead to the formation of stable finite size clusters of NPs on a wide range of sizes, shapes and inner structures. Despite a large interest, the formation of NPs multiplets with a given structure and their interactions is still missed understood. From the experimental point of view, the lack of structural studies employing non-distorting techniques and well characterized building blocks is detrimental. In this context, we studied the structure of electrostatic complexes obtained by simple mixing of inorganic NPs of different radius (R) and surface charge with polyelectrolyte chains of different persistence length (L_p).

This systematic study has allowed us to reveal that spherical silica nanoparticles (SiNPs) can be assembled into stable 1D aggregates by complexation with chitosan semi-flexible chains.^[1, 2] In this presentation, I will present a detailed structural study performed by combining SANS, SAXS, light scattering and cryo-TEM of the hybrid complexes obtained in the different regions of this interesting phase diagram. Then, I will point the pivotal role of L_p/R on this anisotropic NPs' organization. Finally, I will present results concerning the extension of this study to gold NPs.^[3]

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Modulating the Coffee-Ring Effect via particle-interface interactions: role of surfactants and dynamic photocontrol of particle patterning

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Any pinned sessile drop containing particles leaves a ring deposit after drying, as almost all particles concentrate at the drop edge. Named after its most common representative, the Coffee-Ring Effect (CRE) is driven by the evaporation-induced flow, transporting particles toward the contact line [1]. Both scientific curiosity for a phenomenologically simple yet not fully understood problem and technological interest for evaporative particle patterning, have recently intensified research toward understanding and controlling the CRE.

A common strategy to control the CRE is to modify the hydrodynamics in evaporating drops. Surfactants are commonly used to affect the flows, typically at concentrations higher than the critical micellar concentration (CMC). Here, we demonstrate that surfactants can lead to controlled particle deposition, at concentrations lower than the CMC. Surfactant-mediated interactions between the particles and the liquid-gas and liquid-solid interfaces, rather than flow patterns alone, define the deposit morphology. For like-charged particle/surfactant mixtures, rings are always observed. For oppositely charged systems, deposits are also rings, but only for low and high surfactant concentrations. Interestingly, for intermediate concentrations, homogeneous disk patterns are obtained due to the surfactant-mediated affinity for the liquid-gas interface. These effects are reproducibly observed for various particle/surfactant systems [2].

Utilizing light and photosensitive surfactants, we remotely tune particle affinity for the liquid-gas interface, enabling us to finely modulate particle deposition. For drops of fixed composition, adjusting the irradiation time leads to a continuous ring-disk transition. Remarkably, deposits can be reversibly switched between disks and rings using successive UV/blue exposures [3].

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Two-Compartments Macroporous Polymer Capsules

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Porous microcapsules are of great interest in diverse applications, ranging from encapsulation for controlled release, to filtration and purification systems in analytical science or to catalyst support.

Here, we demonstrate a novel method to obtain two-compartments microcapsules: the first compartment in the capsule's core, the second inside the porous structure of the capsule's shell.

The microcapsules are produced by microfluidics, using water-oil-water (W/O/W) double emulsion templates. The capsule's shell is formed by UV-polymerization of an oil phase consisting of a mixture of acrylate monomers with a liquid porogen. During polymerization this mixture phase segregates, creating a network of polymer beads permeated by the porogen and polymeric skin that seals the surfaces of the shell. The embedded porogen forms a second compartment permitting the encapsulation of an additional compound. With this method, di-epoxy and di-amine were simultaneously but separately encapsulated inside one single capsule, providing a rich platform for the future design of microcapsule systems for adhesives or self-healing materials.

Furthermore, the shell compartment offers new possibilities of trigger mechanism. Capsules produced with porogens with low boiling point exhibit an explosive behavior when submitted to a thermal shock. We combined these capsules with magnetic particles and used magnetic hyperthermia to achieve the release of the capsules' content within seconds and without over-heating the surrounding matrix.

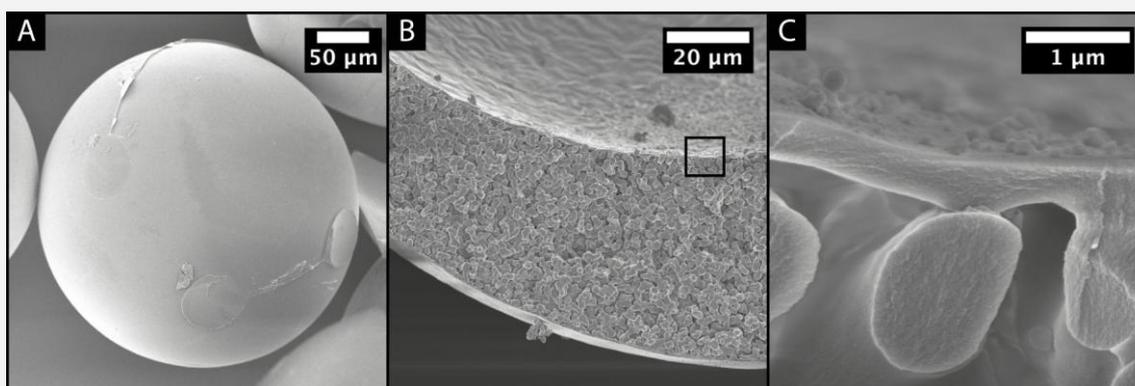


Figure: Two-compartments capsule produced with 15 wt % pentane (A). Cross-section of the shell (B) consisting of a network of polymer beads wetted by the porogen and sealed by a polymer skin (C).

Vesicles-on-a-chip: versatile fabrication of liposomes and polymersomes in microfluidic environment

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Synthetic biology recently appeared as an emerging field of research for mimicking and understanding natural systems from a fundamental point of view. This "bottom-up" approach involves the investigation of the biological and physical properties and mechanisms of functional biological systems (from basic modules/parts of living cells to more complicated systems). One key challenge relies on the fabrication of compartments such as vesicles that can be viewed as model membranes, as demonstrated by numerous studies during the past decades. Despite this fact, reliable methods for high-throughput production of vesicles (liposomes as well as polymersomes) in an easy and well-controlled manner are still in progress. In this scope, we propose a versatile method for producing monodisperse vesicles in a microfluidic environment from double-emulsions templates. The combination of the microfluidic chip design and the original channel treatment as well as the new fluid systems employed in the present study allows the production and manipulation of liposomes as well as polymersomes on demand. This new technique opens a playground for fundamental studies, e.g. on the collective behavior of vesicle clusters and their self-organization, as well as applications such as protein or drug encapsulation and mechanisms of targeted delivery.

Nanoparticle self-assembly in flow

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We investigate the agglomeration of unpolar gold nanoparticles (AuNP) in a laminar liquid flow. Previous batch experiments indicated that temperature determines agglomerate structure. Agglomerates of alkylthiol-stabilized AuNPs were ordered or disordered depending on agglomeration temperature [1].

For the project discussed here, we used a fluidic system (Fig. 1 (a)) at the synchrotron (SOLEIL) to prepare and immediately characterize agglomerates. Agglomeration of AuNPs (6 ± 0.6 nm core diameter) in heptane (approx. 1 g/l) was initiated in continuous flow by mixing with 1-propanol in a static micromixer. The agglomerating sample flowed through an UV/Vis transmission spectrometer and a synchrotron SAXS capillary. The flow setup can provide a steady flux of fresh agglomerates. The age (delay between time where agglomeration is initiated and the analysis time) is tunable from tens of seconds to few minutes.

Temperature-dependent SAXS patterns and UV/Vis absorbance spectra of 6-7 min old agglomerates are presented in Fig. 1 (b) and (c). Agglomerates grown at higher temperatures exhibited more order that caused the emergence of additional peaks in the scattering patterns. We indexed the scattering peaks to a fcc superlattice. Note the difference in surface plasmon resonance between ordered and amorphous agglomerates – crystalline order appears to strongly broaden the peak.

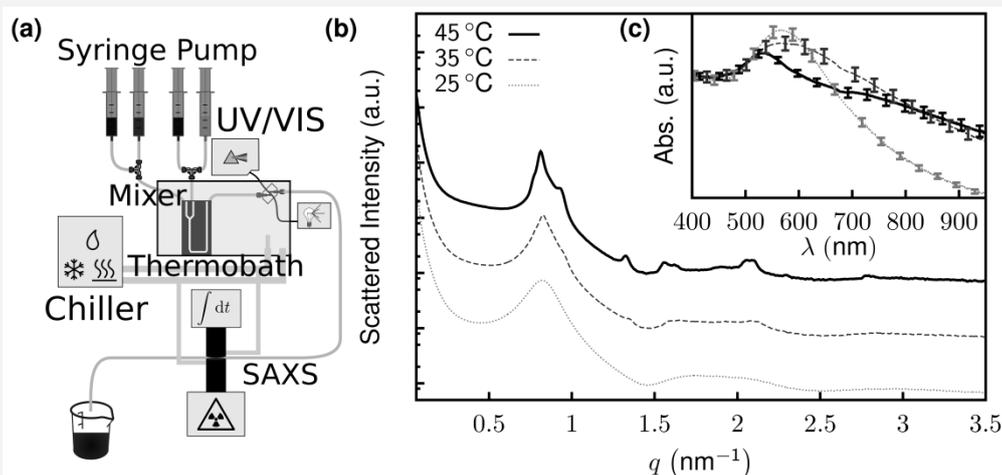


Fig. 1: (a) Illustration of the experimental setup. (b) SAXS patterns after ~ 7 min of agglomeration for different temperatures. (c) UV/Vis absorbance of the samples.

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An instrumented microfluidic tool for complex fluid phase diagram determination: Inline and real-time exploration of solvent extraction.

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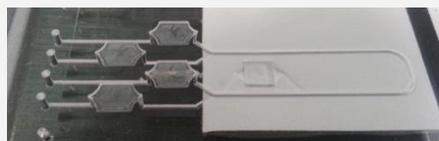
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Liquid-liquid extraction, i.e. control of the reversible transfer of cations between phases, is a core chemical process for metal purification and recycling. The objective of the “REE-CYCLE” project (Rare Earth Element reCYCling with Low harmful Emissions)[1] is to develop the fundamental understanding of complex fluid processing in order to innovate environmentally friendly, economically competitive processes.

The presented work on micro-solvent-extraction takes this approach beyond the state-of-the-art[2]: An instrumented and computer-controlled microfluidic device is described, enabling the first steps towards fast measurement of the free energy of ion transfer between complex fluids[3]. Continuous screening of a manifold parameter set, including e.g. multi-component phase composition, pH, temperature, will be enabled by integrating inline, real-time measurements into a robotized lab-on-a-chip. Miniaturized spectroscopic and sensing methods will allow automated characterization of kinetics/thermodynamics, partition coefficients, chemical potential differences and constituent's activity coefficients.

First results of the microfluidic device, compared to batch mode assays, are presented concerning temperature and pH variation. Examples are shown on N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) reverse micelles diluted in dodecane for lanthanide extraction in the presence of iron. Partition coefficients and kinetics data for different parameters are addressed and resulting pathways explored to enhance separation and selectivity. First data on solvent activity coefficient measurements will also be presented, giving insight on molecule aggregation[4], constituents' chemical potentials and solvent vapour pressure.



Microfluidic device with on-line measurement sites.

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Compartmentalization of Oscillatory Reactions in Liposomes: Toward Chemical Communication

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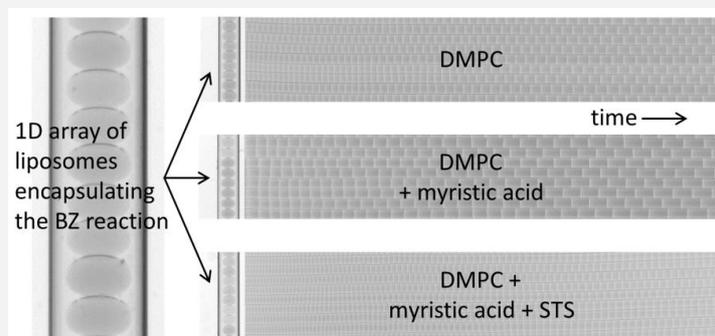
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The generation, propagation and reception of (bio-) chemical information between individual organisms are the keystones of many intelligent communicative systems. For cellular organisms, chemical communication is based on a chemical messenger diffusion/reaction spanning over a wide range of time and length-scales. Here, chemical messengers are able to freely cross biological membranes and be transported to a target by diffusion over larger distances in an aqueous environment. A biomimetic model of such chemical activity can be found in non-equilibrium chemical systems such as the Belousov-Zhabotinsky (BZ) oscillating reaction.¹ The compartmentalization of the BZ reaction in individual reactors, e.g. aqueous droplets or liposomes, can be useful for apprehending short- and long-range chemical communication between neighbouring microreactors.² Herein, we studied using small angle X-ray scattering (SAXS) the effect of BZ species on the lamellarity of phospholipid-engineered membranes in order to rationalize our observations on chemical communication between engineered liposomes encapsulating BZ, prepared in microfluidics and organized into 1D arrays. We show that the communication can be modified upon engineering the properties of the phospholipid membranes using different membrane dopants, which sometimes interact with the species of BZ reaction, thus affecting the communication. A few examples of time-space plots of 1D arrays of liposomes are shown below, displaying the effect on the oscillating behaviour upon doping a DMPC liposome membrane with myristic acid alone or together with tetradecylsulfate.



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Dominance of Non-equilibrium Effects in the Structures of Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface

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Oppositely charged polyelectrolyte/surfactant mixtures control the functionality of many widely used consumer products. Their current physical models at the static air/water interface are set in an equilibrium framework [1]. In contrast, we have linked the interfacial properties of these systems to different non-equilibrium processes that occur in the bulk and at interfaces [2–4].

Here we demonstrate that non-equilibrium effects absolutely dominate the interfacial structures created in such mixtures. We focus on the system poly(sodium styrene sulfonate)/dodecyltrimethylammonium bromide studied using a variety of experimental techniques including neutron reflectometry. We show that the extremely slow equilibration of the bulk means that these colloidal suspensions inevitably exist out of equilibrium. The situation is further complicated by the irreversible formation of liquid crystalline particles in the bulk which can be impervious to dissolution upon chemical change. The formation of these particles depletes the bulk yet their penetration into the interfacial layer modifies the interfacial properties: their retention at the interface affects rheological properties while their dissociation and spreading modifies surface tension. The mechanism of penetration of the particles into the interfacial layer is mediated by different processes: surface affinity, surface trapping and transport under gravity. The static interfacial properties of planar surfaces, droplets and foams are therefore necessarily all different. These factors are not taken into account in the current physical models.

We conclude with a discussion on how a fundamental non-equilibrium understanding of these common mixtures can be harnessed to develop novel triggered delivery applications involving biomacromolecules such as proteins and DNA.

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Sunscreen Formulations and Their Behaviour Upon Thin Film Evaporation

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Sunscreens protect human skin against the detrimental short-term and long-term effects caused by UV radiation, including sunburn, photoageing and photocarcinogenesis. The photochemical behaviour of the active ingredients within a sunscreen formulation has been extensively studied for both organic UV absorber molecules and inorganic particles. Their efficiency is described in the Sun Protection Factor (SPF). However, little is known on how the photostability of sunscreen films is affected when fundamental phenomena such as wetting, dewetting and evaporation are taken into consideration. Herein, an *in vitro* approach has been employed to examine both the deposition patterns and the relevant photochemistry of sunscreen film residues upon evaporation.

The work presented is focused on the UVA-I absorber Avobenzone (AVB) in propane-1,2-diol as the solvent, although the technique is applicable to analysis of a wide variety of UV absorbers. These simple solutions with film thickness ranging from 20 up to 100 μm were deposited on either quartz or Vitro Skin surfaces. Their mass loss, their area change and their UV/vis spectrum were monitored in the open lab air until complete evaporation. The results obtained can explain how film dewetting and precipitation of AVB affect the UV/vis spectrum and thus the SPF upon drying. Our investigation was also extended to liquid films containing nanoparticles and to more complex systems such as particle-stabilised emulsions.

Tuning the properties of silica surfaces by heat treatment

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Due to its plain relevance in nature, industry and technology, silica has been widely used as a component for systems and devices in colloidal and surface science as well as a model substrate for fundamental studies. Specifically it has been extensively used as a substrate for surface force studies, where some discrepancies still exist within the literature data; mostly due to the different preparation techniques used and the history-dependent characteristic of the surface itself. Our work aims to give some insight into this landscape by trying to quantify the effects of different surface treatments and relate them with actual physicochemical parameters.

Forces between single pairs of 5 μm silica colloids have been measured with Atomic Force Microscopy (AFM) colloidal probe technique [1]. The colloids have been subjected to heat treatment at different temperatures (from 1050°C to 1300°C, 2h) and then from the force curves measured, surface parameters such as double layer potential and Hamaker constant have been extrapolated and compared.

The results show that the heat treatment and the temperature at which it is performed affect dramatically the surface properties of the colloids. Upon increasing the temperature both the surface potential and the Hamaker constant increase substantially, for the latter a difference of more than one order of magnitude has been observed going from untreated to 1250°C treated samples. AFM topography and SEM images have been collected in order to verify how the treatment impacts the shape and the topography of the colloids. Our experiments show that upon heat treatment, the surface roughness decrease substantially, in correlation to the observed variation of surface potential and Hamaker constant.

In conclusion, our work demonstrates how an appropriate and controlled heat treatment can be used to tune the roughness of silica surfaces, consequently modulating their interfacial behaviour.

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DYNAMIC PROPERTIES, FOAMABILITY, FOAM STABILITY AND SURFACE RHEOLOGICAL BEHAVIOUR OF SURFACTANTS - THE BASIS FOR A DEEPER UNDERSTANDING OF THEIR INDUSTRIAL APPLICATIONS

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Introduction

The behaviour of surfactants in various industrial applications is often related to their diffusion and adsorption at gas/liquid and liquid/liquid interfaces. Knowledge of the equilibrium properties such as static surface and interfacial tension provides only limited information in the case of time-dependent processes. Processes in which 'new' interface is generated in fractions of a second are significantly influenced by the dynamic behaviour of the surfactants involved. Under these conditions, dynamic surface and interfacial tension become more important in the understanding of the functionalities of surfactants such as wetting and immersion, emulsification and dispersion or foaming and defoaming. Additionally, the elastic and viscoelastic properties of interfaces are important for a variety of industrial applications. This is why foamability and foam stability as well as the interfacial rheological properties can also provide important information.

Materials and Methods

This paper investigates surfactants with low to good foam formation tendencies (nonionic surfactants as linear and branched chain alcohol ethoxylates and alcohol EO-PO/BO adducts which are commercially available). In order to describe the properties of these surfactants with different hydrophobic/hydrophilic characteristics, we have applied different methods. The static behaviour of surfactants was investigated using the well-known tensiometry measuring methods to determine the static surface tension and the critical micelle concentration values. To study the dynamic behaviour of surfactants, we used the maximum bubble pressure method to determine their dynamic surface tension and the diffusion coefficients. The foaming and stability behaviour of the surfactant solutions were characterised using maximum foam height and optical foam structure measurements. The interfacial rheological properties of the surfactants used were studied by the oscillating spherical drop method. In this method, the pressure resulting from the surface tension at a curved surface is measured in a spherical drop that is oscillating sinusoidally. In solutions of surface-active substances, the surface tension is calculated from the pressure as a function of time and surface area. From the surface tension curve, the complex interfacial dilatational modulus E^* , the elastic modulus (storage modulus) E' as well as the viscous modulus (loss modulus) E'' can be determined. The relationship between these parameters is: $E^* = E' + iE''$. E^* is a measure of the total resistance of the surface to deformation.

Results

The results of static and dynamic surface tension data (surface tension and diffusion coefficient data) of the linear and branched alcohol ethoxylates and the alcohol EO-PO/BO-adducts as a function of temperature will be presented. We will discuss the results of diffusion coefficient and cmc-determination in relation to the chain length and number of EO/PO-adducts. The results of the foam and surface elastic properties of nonionic surfactants as a function of concentration and chemical structure will also be presented. A relationship between E^* and the foam stability will be demonstrated for the selected surfactant systems. The study and analysis of dynamic interfacial tension data of commercially available surfactants leads to correlations using models of surfactant adsorption kinetics which assist in finding the 'best' surfactant. It also clarifies in which application(s) the surfactant could offer optimum performance.

Characterisation of Sulphonated Methyl Esters in the Bulk and at the Air-Water Interface

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Sulphonated methyl esters (SME) have been growing for the last ten years and currently stand at more than ten percent of the total linear alkyl-benzene sulphonates (LAS) production. It is an environmentally friendly alternative of LAS and irrespective of the current crude oil pricing situation is considered as a viable replacement of LAS. Despite their wide usage, mainly in cleaning formulations, their physical characteristics published in the literature often differ, sometimes up to order of magnitude. The lack of clarity on their physical properties has been one of the limitations for increasing the scope of their applications. To address this issue, we investigated the SME homologous series (C12, C14, C16, C18) with regard to their surface tension (Fig. 1), adsorption properties; critical micellization concentration; micelle aggregation number and ionization degree, and the effect of added salt [1]. Data on the foaminess of SME solutions and foam stability will be also reported.

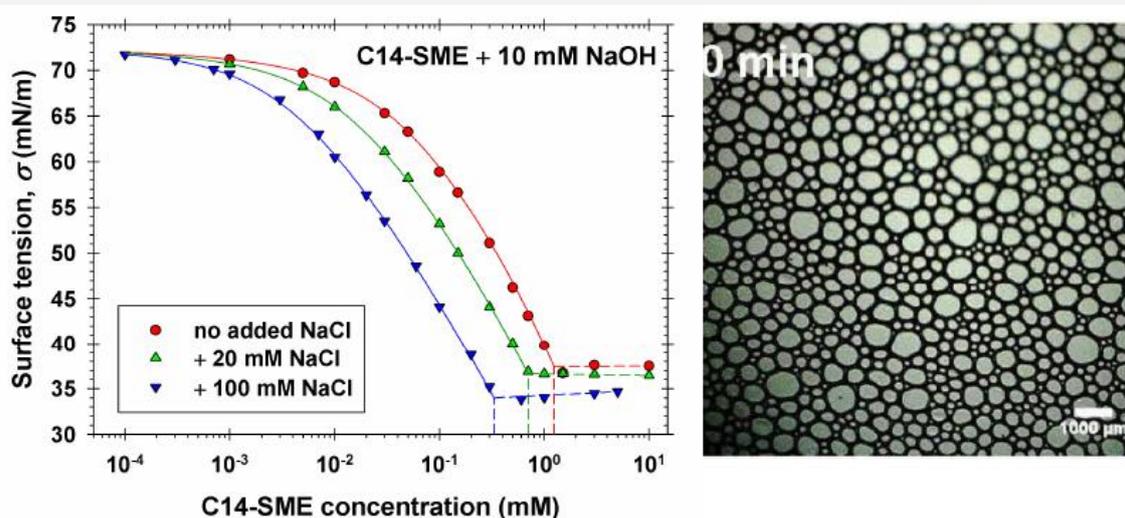


Fig. 1. Surface tension of C14-SME solutions (left) and the produced foam (right).

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Quatsomes: New Highly Stable Nanovesicular Structures

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There is a large interest in finding non-lipid building-blocks or tectons, which self-assemble into stable vesicles, and which satisfy the quality standards required in pharmaceutical formulations.¹

Here we show the ability of quaternary ammonium surfactants and sterols to self-assemble forming stable amphiphilic bimolecular building-blocks with the appropriate structural characteristics to form, in aqueous phases, closed bilayers, which we named quatsomes. These colloidal structures are stable for periods as long as several years, their morphology do not change upon rising temperature or dilution, and show outstanding vesicle to vesicle homogeneity regarding size, lamellarity and membrane supramolecular organization.² Phase behavior analysis of different aqueous mixtures of the quaternary ammonium surfactant CTAB and cholesterol have shown that a pure vesicular phase is only formed at equimolar proportions of both components, whereas coexistence of vesicular structures with other types of colloidal and crystalline phases is observed when one moves away from the equimolar ratio.³ Molecular dynamic simulations revealed that the cholesterol and CTAB pair works as a unique supramolecular architecture for the formation of more complex colloidal phases such as vesicles.

Many functionalities can be implemented simultaneously in quatsomes,⁴ either by covalent attachment to sterol like molecules, by electrostatic interaction with the cationic ammonium head of surfactant units or by hydrophobic interaction with the bilayer. These possibilities open a broad range of applications in pharmacy, cosmetics and materials synthesis.

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Synergy in extraction system chemistry: combining configurational entropy, film bending and perturbation of complexation

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Solvent extraction relies on controllable distribution of electrolytes between two complex fluids. In the “ieanic” approach, one replaces competing stoichiometric complexes, by steps in free energy; the motor of the extracting system, that are organized solvent phases¹.

It is known that synergy effects rely on cooperative phenomenon, and are the source of the selectivity. Using classical supra-molecular and organo-metallic approach, in principle, the nature of the solvent should not influence the selectivity curve. But in practice, it does, as can be seen on figure 1.

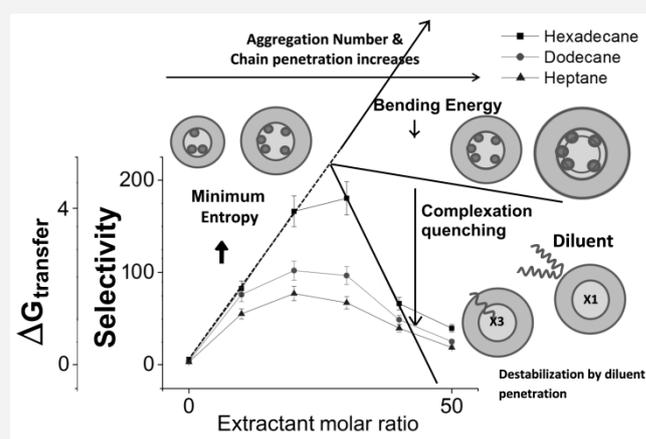


Figure 1: The synergy plot relying the double difference in free energy of transfer to the mole fraction of the two combined in three different solvent².

We will show on two different examples how universal phenomena such as complexation configurational entropy, extractant film bending energy and perturbation of complexation by solvent penetration combine. By looking at the diluent effect, with combined surface tension, ion concentration and scattering studies, we propose a coherent mechanism to explain synergistic extraction. ***This new explanation is the first to our knowledge that predicts the non-linearity observed when penetrating and non-penetrating solvents are mixed.*** Therefore, the knowledge of the mechanism linked to solvent effect helps formulation in complex systems containing seven to nine components as studied within the ERC project REE-CYCLE³.

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³ ERC REE-CYCLE 2013-2108

The Role of DNA in the Formation of Metallic Nanoparticles in Lyotropic Liquid Crystals

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Metal nanoparticles have attracted a lot of attention in the field of colloidal and material science due to their unique electronic and optical properties, which are dominated by the localized surface plasmon resonance. Because of the broad field of potential applications there is also a growing interest in developing new green methods for the controlled synthesis of the nanomaterials. Due to the rich polymorphism, lyotropic liquid crystals formed by amphiphilic molecules are particularly interesting templates to control size and morphology of nanoparticles.

In the present work we report the synthesis of silver nanoparticles in the various lyotropic liquid crystalline phases formed by biologically friendly surfactants with or without cationic surfactant-DNA complexes in aqueous solution with different additives [1-2]. Two different preparative strategies have been applied. Firstly, surfactant molecules have been used to form the liquid crystalline phases in aqueous solution as well as to reduce the silver ions into silver atoms as confirmed by FTIR and ¹H NMR spectroscopy. Secondly, by using DNA-containing liquid crystals silver nanoparticles were synthesized via photoreduction of the DNA-Ag⁺ complexes where the DNA itself may act as template.

The effect of the formation of silver nanoparticles on the lyotropic liquid crystalline phase was investigated with small angle X-ray scattering, polarizing optical microscopy and ²H NMR spectroscopy. On the other hand, the influence of the template mesophase (which may or may not contain DNA) on the formation rate and nanoparticle size and morphology is studied using UV-spectroscopy, TEM and AFM.

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Effect of supporting cushion materials and deposition conditions on the formation of POPC/POPE lipid bilayers

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Formation of supported lipid bilayers on soft polymer cushion has been extensively studied in recent years due to their numerous potential applications for biotechnology as cell-membrane models, for biosensors, drug delivery systems or as platforms for cells. However, the SLB formation on cushion material is not fully understood. The explanation of the mechanism of SLB formation after exposure of small lipid vesicles on polyelectrolyte multilayers still needs some improvement since it depends on many factors.

In our studies we have focused on the formation of complete supported lipid bilayers in relation to deposition conditions of vesicles and underlying cushion assembled from various polyelectrolyte multilayers. Lipid vesicles were formed from zwitterionic 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) and 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphoethanolamine (POPE) in phosphate buffer with or without NaCl addition. Three various pH values of buffer were also investigated. Polyelectrolyte cushions with different number of layers, applied as a support for lipid bilayer, were constructed by the *layer by layer* deposition of polycations (PEI, PLL, PDADMAC) and polyanions (PGA, PSS) on quartz or silicon surface. By combining the quartz crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM), we have investigated the process of the formation of SLB on polyelectrolyte films in dependence on the pH and addition of NaCl in the buffer solution and the type of the cushion. We have found that all studied factors affected SLB formation and its quality. We have also discovered that the amount of water entrapped within polyelectrolyte cushion plays a crucial role in bilayer formation. Moreover, the degree of hydration of polymer film induced the kinetics of bilayer growth. Finally, we can control the lipid structure at the surface.

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Surfactant-free CO₂-based microemulsion

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Microemulsions are considered a very versatile reaction media with many applications ranging from nanoparticle templating to preparative organic chemistry. In order to be more environmentally friendly, efforts are directed towards the formation of microemulsion with less quantity of surfactants. Even though, surfactant-free microemulsions have already been known since the late 70s, only scarce papers deal with this topic.^[1] The other main problem of conventional microemulsions is the separation and removal of solvent from products. This problem can be overcome using microemulsions with compressed fluids. Compressed CO₂ and water represent extremes of the solvent spectra, therefore microemulsions made with these two components can be regarded as universal solvents.^[2]

Here we present for the first time a surfactant-free microemulsion composed of water, acetone and cCO₂.^[3] Raman spectroscopy has been used to get insights about the state of aggregation of water molecules in this ternary system at high pressure. It was demonstrated the presence of two nanodomains of clearly different composition: water-rich nanodomains and CO₂-expanded acetone rich nanodomains. This nano-structured liquid has the capacity to dissolve hydrophobic compounds, such as ibuprofen, in the presence of large amounts of water. This finding opens new opportunities in the fields of confined reactions and material templating.

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Quantitative Study of Patterned Microcontact Printed Self Assembled Monolayer with Imaging Ellipsometry

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Approximately 20 years ago the Whitesides Group (1993) described microcontact printing (μ CP) as a tool to transfer an “inked” material from elastomeric material onto flat substrates. In the beginning this technique was used as a method to pattern gold surfaces. Both easy handling in fabricating patterned surface and variation of the substrate and inked material this technique became significant in patterning surfaces.

Here we present a quantitative study of patterned microcontact printed SAM of Octadecyltrichlorosilane (OTS) on silicon dioxide surface with Imaging Ellipsometry. The patterned silicon wafers were characterized with Imaging Ellipsometry (Accurion, EP4-SE). Therefore Delta and Psi maps were recorded at 25 different points for each wafer (10x objective, AOI = 50° and Lambda = 500 nm). Especially Delta is more sensitive compared to Psi which is typical for thin transparent films. The thickness of the patterned SAM was obtained by a fitting process using EP4-Model, Accurion and transferred the Delta maps (Figure 1, a) into a thickness maps (Figure 1, b) by interpolation of Delta. These maps were analyzed quantitatively in terms of homogeneity and quality of the patterning (Figure 1, c). Imaging ellipsometry is a fast, non-destructive and sensitive technique compared to AFM, which is important for observing large areas regarding the quality and thickness of micro-patterned surfaces..

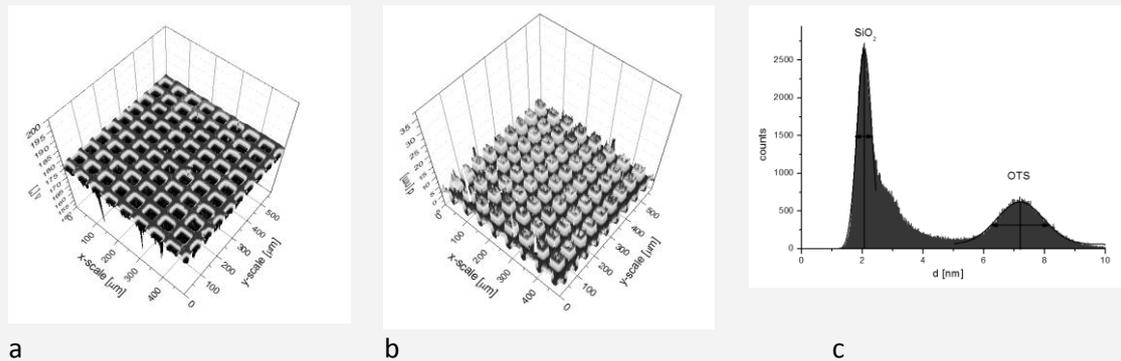


Figure 1: Delta ($\lambda= 500$ nm, AOI= 50° , 10x objective) (a), calculated thickness (b) map of micropatterned OTS on SiO₂/Si and Histogramm-plot (c) of thickness map including a Gaussian Fit to determine the thickness of the substrate (d (SiO₂) = 2.09 nm, $\sigma = 0.51$ nm) and layer thickness of OTS (d (OTS) = 5.11 nm, $\sigma = 1.50$ nm).

When Lipid Tails and Sterol-like Structures are Covalently Linked: Unique Aggregation Behavior of a Bacterial Bolaform Lipid

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To improve their resistance to antimicrobial agents, some bacteria have developed lipopolysaccharides (LPS), whose glycolipid portion, the lipid A, presents very long-chain fatty acids (VLCFA), able to span the entire profile of the external membrane of the bacterial wall. In a recent study, we found that the *Bradyrhizobium* BTAi1 strain builds a unique lipid A in which the VLCFA terminus is covalently linked to a hopanoid structure (HoLA) [1]. Hopanoids, pentacyclic triterpenoids, display structural similarity with eukaryotic sterols and are thought to stabilize membranes, control fluidity and permeability and bolster the integrity of bacterial cell envelope.

In this contribution we present the results of a physico-chemical investigation on the peculiar microstructural and dynamic properties of HoLA-enriched lipid bilayers. Initially, symmetric bilayers were prepared and characterized. Successively, we set up a procedure to prepare asymmetric liposomes in which HoLA is present only in the external leaflet, similarly to what happens in bacterial membranes.

The investigation was performed using an experimental strategy which combines dynamic light scattering (DLS) to estimate liposome dimension, small angle neutron scattering (SANS) to estimate the thickness of the lipid bilayer, electron paramagnetic resonance (EPR) to investigate the dynamics of the lipid hydrophobic tail in the bilayer and differential scanning calorimetry to investigate bilayer phase transition.

Our results demonstrate the unique capability of the hopanoid moiety to rigidly anchor the terminus of the VLFA among the acyl chains of the apposing lipid leaflet, constituting a sort of "tightrope" between the two membrane surfaces and finally leading to enhanced mechanical strength and stabilization of the membrane. Besides their biological relevance, our results open a wide range of biotechnological applications.

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