

Surface active monomers: tools for the synthesis of functionalized monodisperse polymer nanoparticles

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Polymeric nanoparticles presenting functional surfaces have been extensively studied due to their increased reactivity and wide range of possible applications, especially in the field of biotechnology. Surface active monomers (also known as “surfmers”) are molecules that combine the functionalities of surface activity, polymerizability and reactive groups, so that a surfmer acts as both surfactant and monomer. Hence, during emulsion polymerization processes, surfmers are mostly on the particles’ surface and are directly incorporated into the particles’ polymeric backbone. Consequently, their use leads to an increase in the particles’ stability while allowing for the controlled display of the functional groups on the particles’ surface. The present work presents the synthesis of two surfmer molecules and the preparation of polystyrene (PS) and poly(methyl methacrylate) (PMMA) nanoparticles having either active ester or isothiuronium groups on the surface. The nanoparticles were prepared through miniemulsion polymerization and the surfmers were used as the only surfactants and as comonomers. With this approach, monodisperse nanoparticles with a reactive surface functionality were obtained. The surfmer molecules were synthesized and characterized through nuclear magnetic resonance, infrared spectroscopy and elemental analysis. Then, polymeric nanoparticles were produced through miniemulsion polymerization and the syntheses were optimized by varying reaction parameters and reagent concentration in order to obtain reproducible and stable colloidal dispersions. The resulting particles were characterized through photon correlation spectroscopy and scanning electron microscopy and data revealed monodisperse particle systems with tailored size ranging from 60 to 180 nm. Micro-electrophoresis and conductometric titrations were used to determine and quantify the presence of the functional groups in the particles’ surface, before and after a hydrolysis process. In conclusion, functionalized particles can be easily produced through this route and tailored for conjugation with biomolecules. The configured particles with customized functional surfaces are promising candidates for multifunctional platforms suitable for biomedical applications.

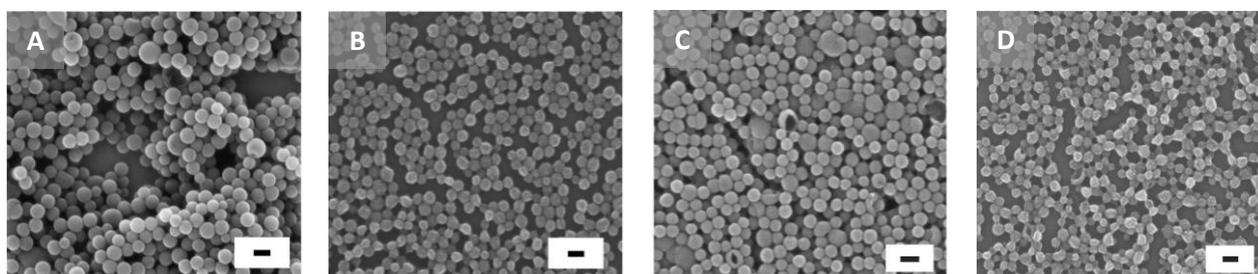


Figure 1 SEM images of PS particles (A and C) and of PMMA particles (B and D) synthesized via miniemulsion polymerization using surfmer molecules carrying either the functional groups of an active ester (A and B) or of an isothiuronium (C and D). These optimized formulations show a monodisperse dry particle size distribution from 50 to 100 nm. Scale bar represents 100 nm.

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Supracolloidal association of microgels and supramolecular tubules of bile salt derivatives

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The aggregation of colloid-sized particles is a fascinating subject, widely employed in chemistry, physics, and biology. The formation of supracolloidal nanostructures represents nowadays an intriguing approach for building novel artificial nanomaterials and devices [1]. In general, to master a fine control over the interactions of colloidal particles is fundamental when approaching complex structures. This control is particularly crucial when involving systems of particles of different shapes, where specific interactions can be exploited to provide complex supracolloidal geometries with expanded application potential. With this background, we have studied supracolloidal aggregation between spherical microgels and supramolecular surfactant tubes. The interactions were controlled by changing charge of the particles and parameters such as electrolyte concentration and temperature. We used cationic or anionic microgels and catanionic surfactant tubes with tunable charge, which were formed in mixtures of anionic and cationic derivatives of bile salts [2]. The charge of the tubes was controlled by changing the anionic/cationic derivative molar ratio. A structure of triangular rolled layer was observed for the catanionic tubes; with the edges of the layer creating a spiral pattern along the tubular walls. Tubes with a smooth surface were instead formed in the self-assembly of only the anionic derivative. We demonstrate in this work that the microgels interact specifically to the edges of the layers that form the tubular structures. By properly choosing the tube type and adjusting the interaction conditions, virus-like particles, microgel-decorated tubules or clusters of tubes interconnected by microgels were formed (Figure 1a, b and c, respectively). Extended forms of these clusters provide a basic framework of new low-density hybrid gels.

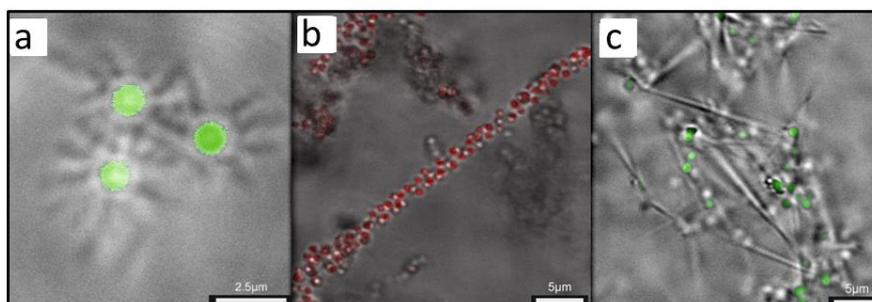


Figure 1 Virus like particles with a microgel core and a corona of tubes (a), microgel decorated tubes (b), clusters of tubes interconnected by microgels (c).

Acknowledgements. The financial support of European Soft Matter Infrastructure (ESMI) is acknowledged

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Polyelectrolyte/surfactant complexes (PESCs) – some interesting structural and rheological behaviour

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Mixtures of polyelectrolytes and surfactants typically form polyelectrolyte/surfactant complexes (PESCs), especially if they are oppositely charged. Such complexes can vary largely with respect to their structures [1] and also with respect to their rheological properties. These properties depend largely on the type of aggregate formed by the surfactant and the properties of the polyelectrolyte, such as chain stiffness and charge density – and, of course, on the mixing ratio and the total concentration.

In our experiments we focused on polysaccharide based polyelectrolytes (hyaluronic acid (HA), cationically modified cellulose (JR400), chitosan, etc.) and combined them with oppositely charged surfactants, but we also compared our results then to polyelectrolytes like polyacrylate (NaPA), which have a much lower rigidity of the polyelectrolyte chain. We stayed in the rather dilute regime (0.25-1 wt% of polyelectrolyte) and our focus was on the polyelectrolyte rich side of the systems, although we also explored the surfactant excess regime [2]. Such PESCs show precipitation in the range of equimolar mixing, which depends quite markedly on the type of polyelectrolyte employed – and also on the salinity of the systems. However, even more these PESCs may differ in their rheological behavior, where in some cases the addition of small amounts of surfactant leads to an increase of viscosity by 4 orders of magnitude [3], while in other cases the viscosity remains constant, or is even reduced. This rheological behavior was linked by us to the mesoscopic structure as probed by static and dynamic light scattering (SLS, DLS) and in particular small-angle neutron scattering (SANS) and complementary cryo-TEM, while some additional insight into the mesoscopic dynamics of these systems was gained from neutron spin-echo (NSE) experiments.

Formation of interconnected and extended PESC aggregates is typically the source for much enhanced viscosity and interestingly this is coupled to an intermediate stiffness of the polyelectrolyte. For more flexible chains compacted aggregates are observed, while the very stiff and weakly interacting HA forms rather large and well-defined aggregates already at very low surfactant concentrations. But it also only able to bind a small amount of surfactant in these aggregates, which have an interesting internal hybrid structure of locally rod-like arrangement, that hasn't been reported so far for PESCs [4]. Another interesting finding is the fact that the local dynamics of polyelectrolyte chains in PESC aggregates as seen by contrast variation NSE might be rather little affected by the overall structure of these aggregates [5].

In summary, we observe that the structural arrangement in PESCs can be explained in a rational way via the properties of the polyelectrolyte and the self-assembly behavior of the surfactant. Based on the PESC structure one can then also explain and optimize the rheological properties.

Acknowledgements The financial support of the BMBF (project No. 05K13KT1) is gratefully acknowledged.

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Drying aqueous colloidal systems: molecular interactions, self-assembly and homeostatic behavior

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Evaporation is a ubiquitous process in aqueous systems, which may be advantageous for processing materials through drying or deadly for living systems. Since surfactants, polymers and particles are usually non-volatile, water evaporation will lead to the build-up of concentration gradients in the system, from the air/liquid interface into the dispersion's bulk. These concentration gradients will in turn generate structuration gradients in the colloidal system, which lead to changes notably in transport properties along the gradients. We will show that such a feedback loop on water evaporation can lead to non-linear behaviors, which are crucial for land-living animals' survival and opens new avenues in drying and filtration processes.

We designed millifluidic drying cells, which consist of a small capillary attached to a large reservoir, with one tip exposed to air at a controlled relative humidity. Chemical potential boundary conditions are thus set and controlled during drying. We monitored drying with time with a combination of mapping techniques: polarized microscopy, infra-red microscopy and coherent small-angle scattering, which yields both concentration and structuration gradients. We also measured independently the evaporation rate through gravimetry.

Using simple surfactant aqueous solutions, we show that the evaporation rate is nearly independent of water evaporation driving force, the air relative humidity [1]. Strikingly, this behavior is identical to that of stratum corneum, skin's outer layer. We demonstrate that this non-linear behavior stems from the feedback loop on water transport. Drier air should lead to a higher evaporation rate due to an increased chemical potential difference between the air and the solution. However, this variation is absorbed in a very thin and dry phase at the air/water interface. This phase corresponds to dramatically low water diffusion coefficients, which in turn efficiently decrease water evaporation [2]. Uncovering the mechanism of this homeostatic behavior opens new strategies to evaluate the impact of a formulation on skin, lung or tear films.

We will also show that this mechanism becomes relevant when drying, or filtering, dispersions of interpenetrable colloids, such as microgels or "hairy" particles [3]. Indeed, large changes in water chemical potential and permeabilities will occur in the concentrated regime, in contrast to the drying of more conventional colloidal dispersions. Taking these molecular interactions into account is crucial for the processing of more complex, and thus realistic, colloidal dispersions into materials.

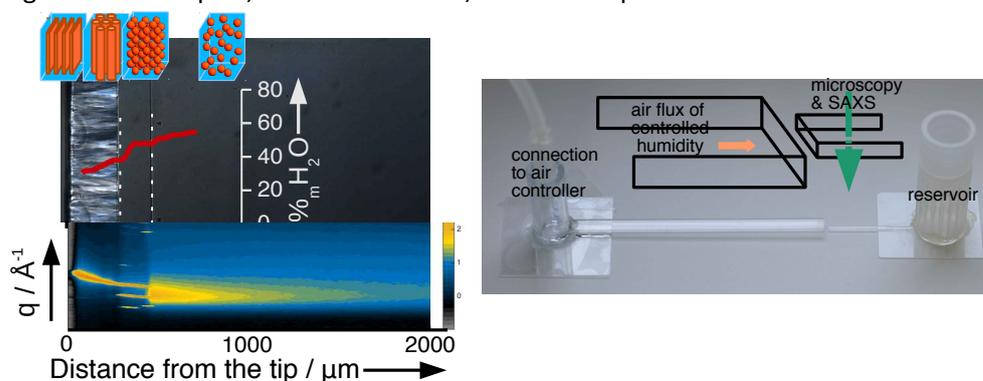


Figure 1: Left: experimental monitoring of composition and structural gradients through microscopy, infra-red microscopy and small angle-scattering; Right: capillary cell for controlled drying

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Assembling Oppositely Charged Lock and Key Responsive Colloids: A Mesoscale Analogue of Adaptive Chemistry

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We have seen a considerable effort in colloid sciences to copy Nature's successful strategies to fabricate complex functional structures through self-assembly. This includes attempts to design colloidal building blocks and their intermolecular interactions such as to create the colloidal analogues of directional molecular interactions, molecular recognition, host-guest systems, and specific binding [1]. Here we show that we can use oppositely charged thermoresponsive particles with complementary shapes such as spheres and bowls to implement an externally controllable lock and key self-assembly mechanism. The use of tuneable electrostatic interactions combined with a temperature dependent size, shape and van der Waals interactions of these building blocks provides an exquisite control over the selectivity and specificity of the interactions and self-assembly process. The dynamic nature of the mechanism allows to reversible cycle through various structures that range from weakly structured dense liquids to well-defined molecule-shaped clusters with different configurations through variations in temperature and ionic strength. We link this complex and dynamic self-assembly behaviour to the relevant molecular interactions such as screened Coulomb and van der Waals forces and the geometrical complementarity of the two building blocks, and discuss our findings in the context of the concepts of adaptive chemistry recently introduced to molecular systems.

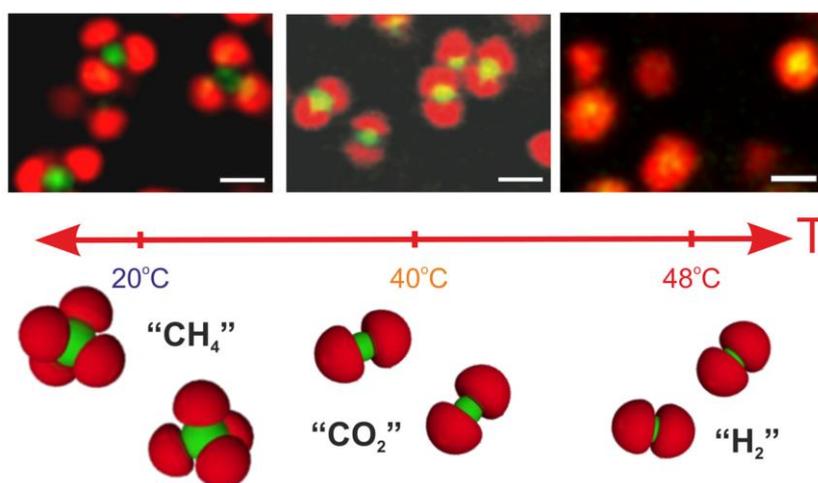


Figure 1 Influence of the temperature on the lock and key self-assembly into colloidal molecules with adjustable valency. 2D CLSM micrographs of a dispersion ($c_L=1$ wt%, $N_L/N_K \sim 6$) and schematic representations illustrating the specific self-assembly in colloidal molecules with a valency ~ 4 at 20°C ("methane", CH₄, configuration, left panel). Increasing the temperature to 40°C, the key- particles exhibit a collapsed state and the valency of the assembly decreases to ~ 2 ("carbon dioxide", CO₂, configuration, central panel). When both the lock- and key- particles are in their collapsed state at 48°C, key- microgels are confined between two lock- particles ("dihydrogen", H₂, configuration right panel).

Topological defects in liquid crystals as templates for molecular self-assembly

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Topological defects in liquid crystals (LCs) have been widely used to organize colloidal dispersions and template polymerizations, leading to a range of elastomers and gels with complex mechanical and optical properties. However, little is understood about molecular-level assembly processes within defects. This presentation will describe how nanoscopic environments defined by LC topological defects can selectively trigger processes of molecular self-assembly. By using fluorescence microscopy, cryogenic transmission electron microscopy and super-resolution optical microscopy, key signatures of molecular self-assembly of amphiphilic molecules in topological defects are observed - including cooperativity, reversibility, and controlled growth of the molecular assemblies. By using polymerizable amphiphiles, we also demonstrate preservation of molecular assemblies templated by defects, including nanoscopic “o-rings” synthesized from “Saturn-ring” disclinations. Our results reveal that topological defects in LCs are a versatile class of three-dimensional, dynamic and reconfigurable templates that can direct processes of molecular self-assembly in a manner that is strongly analogous to other classes of macromolecular templates (e.g., polymer—surfactant complexes). Opportunities for the design of exquisitely responsive soft materials will be discussed using bacterial endotoxin as an example.

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Unconventional gels made of self-assembling DNA nanostars

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The realization of smart biomaterials, i.e. purposely-designed materials whose properties can be reversibly modulated by external stimuli, is nowadays pivotal in many research fields. In this context, DNA has rapidly emerged as a promising basic element due to its natural ability to self-assemble in a thermo-reversible and controlled fashion. Here we show how DNA nanoconstructs, i.e. DNA-made nanoparticles with tunable valence and strength of interaction, can be smartly-designed to programme not only their shape but also their collective thermal behavior. Specifically, we present an unconventional DNA hydrogel, made of self-assembling DNA nanostars, having the unprecedented peculiarity of melting both upon heating and upon cooling [1]. The possibility of creating a bulk material that reversibly gels by heating was firstly proposed in [2]. In this theoretical model, composed by a mixture of tetravalent (A) and monovalent (B) patchy particles, the presence of two different bonding arrangements, i.e. entropically-favoured AA bonds and energetically-favoured AB bonds, leads to a competition between two possible low-temperature structures: a percolating network of bonded A particles (gel) or a fluid of diffusing AB₄ aggregates (in which the four patches of an A particle are completely saturated by B particles). Under specific conditions, this system undergoes a fluid-gel-fluid transition upon cooling and it exhibits a re-entrant phase-separation (Safran's like phase-diagram [3]). To experimentally reproduce the model, we used, as A particles, tetravalent DNA nanostars [4] and, as B particles, 6-base-long DNA competing sequences. Our results confirmed the predicted behavior: an extremely viscous gel (indicated by a remarkable slowing down of the relaxation time measured by dynamic light scattering) is present only in a narrow range of temperatures, while the system behaves as a fluid outside this window. Furthermore, the experimental phase-diagram shows the anticipated re-entrant shape, signalling the presence of competitive interactions. We thus discuss how to exploit the versatility of DNA nanoconstructs to conceive and develop smart biomaterials with programmable properties and unusual temperature behaviors.

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Floating Lipid Bilayers at the Liquid/Liquid interface

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Biological membranes are vital components of all living organisms. They form the boundaries between the various compartments of cells and constitute platforms for essential biochemical processes like enzymatic reactions, molecular transport, or the formation of functional lipid domains. Importantly, structural insight is often a prerequisite to understand the details of these processes. X-ray and neutron reflectometry enable the structural characterization of model biological membranes at sub-nanometer resolution and the investigation of interactions of membranes with a variety of biomolecules [1]. This has only become possible with the simultaneous development of methods for membrane immobilization in planar geometries, such as solid-supported membranes or membranes floating on polymers, lipids, or soft tethers [1,2]. However, when using these approaches, studies on molecules crossing the membrane or deeply penetrating into the bilayer chain region (see toxins, amyloid peptides, membrane proteins in general) turned out to be difficult, because membrane mobility often suffered from the presence of the solid surface. In fact, the water gap beneath solid-supported floating membrane is rarely thicker than 2nm.

Here we present an alternative route, the immobilization of lipid membranes near functionalized liquid/liquid (L/L) interfaces. The latter are intrinsically soft, self-healing, defect-free and the replacement of the solid support with a liquid phase enables manipulation of the interface through both liquids. Negatively charged lipid bilayers were immobilized via vesicle fusion onto oil/water interfaces functionalized with positively charged lipids and structurally investigated using specular neutron reflectometry. The interaction between the bilayer and the L/L interface was tuned by variation of the ionic strength, as evidenced by a bilayer displacement relative to the interface (Figure 1).

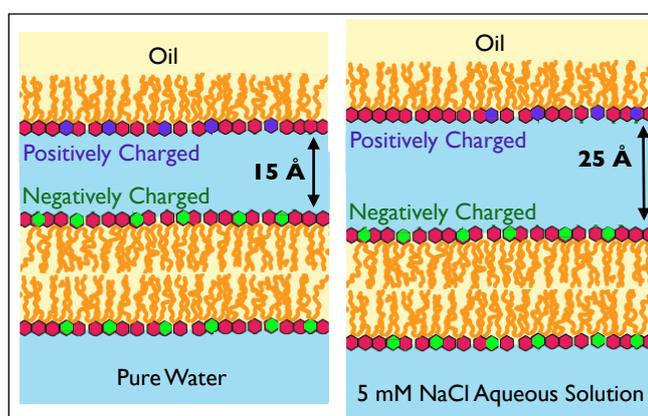


Figure 1 Schematic representation of a negatively charged lipid bilayer adsorbed onto a pre-functionalized L/L interface before (left) and after (right) increasing the ionic strength of the aqueous phase.

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Reshaping, Assembly, and Applications of Gold Nanoparticles Assisted by Femtosecond Pulse Lasers

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The vast majority of the outstanding applications of gold nanoparticles (Au NPs) developed during the last two decades have arisen from their unique optical properties. Within this context, rational synthesis and assembly of Au NPs have been the main research focus, aiming at the design of nanoplasmonic devices with tailored optical functionalities. The progress made in this field is thus to be ascribed to the understanding of the origin of the interaction between light and such gold nanostructures, the dynamics of which have been thoroughly investigated with significant contributions from short and ultrashort pulse laser technologies [1].

We focus this presentation on the potential of pulse lasers to provide new fundamental insights into the electron dynamics involved in the interaction of light with the free conduction electrons of Au NPs, that is, localized surface plasmon resonances (LSPRs). The excitation of LSPRs with a femtosecond pulse laser is followed by thermalization of the Au NP electrons and the subsequent relaxation of the nanocrystal lattice and the surrounding environment, which generally results in surface melting [1]. These concepts have been exploited toward the preparation of highly monodisperse Au NPs via pulse laser irradiation of non-uniform gold colloids. The applicability of pulsed coherent light has been extended toward the direct synthesis and manipulation of Au NPs. Through ablation of a gold target in a liquid with pulse lasers, spherical Au NPs can be synthesized with no need of stabilizing ligands. In addition, femtosecond laser irradiation has been proven a unique tool for the controlled welding of plasmonic gold nanostructures by electromagnetic field enhancement at the hot spots of assembled Au NPs [2]. The combination of such nanostructures with pulse lasers promises significant chemical and biochemical advances [3], including the efficient photothermal destruction of cancer cells avoiding damage of surrounding tissue [4].

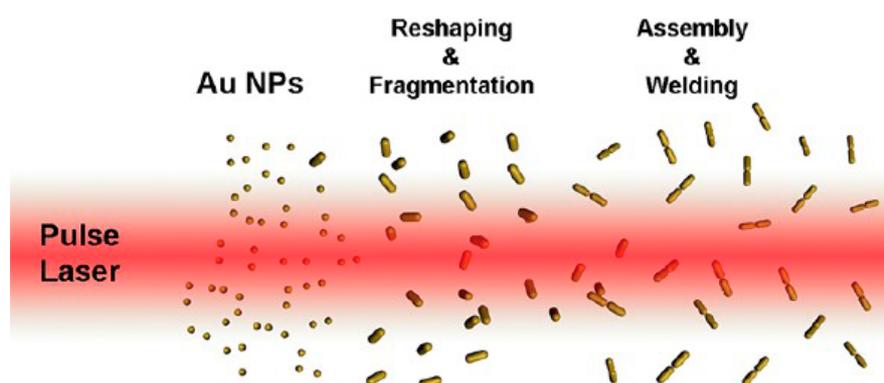


Figure 1. Reshaping and Assembly of Gold Nanoparticles Assisted by Femtosecond Pulse Lasers

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Standing-wave x-ray fluorescence enables near-angstrom precision depth localization of biologically relevant chemical elements in molecular layers

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In nature, biomolecules are often organized as functional thin layers in interfacial architectures, the most prominent examples being biological membranes. Biomolecular layers play also important roles in context with biotechnological surfaces, for instance when they are the result of adsorption processes. For the understanding of many biological or biotechnologically relevant processes, detailed structural insight into the involved biomolecular layers is required. Here, we use standing-wave x-ray fluorescence [1, 2] to localize chemical elements in solid-supported lipid and protein layers with near-Angstrom precision. The technique complements traditional specular reflectometry experiments which merely yield the layers' global density profiles. While earlier work mostly focused on relatively heavy elements, typically metal ions, we show that it is also possible to determine the position of the comparatively light elements S and P, which are found in the most abundant classes of biomolecules and are therefore particularly important [3, 4]. This work may constitute the basis for the label-free, high-resolution, element-specific structural investigation of complex biomolecular layers and biological surfaces.

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Interdependence of Double-Layer and Depletion Forces between Charged Surfaces in the Presence of Like-Charged Polyelectrolytes

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Long-ranged oscillatory forces arise between charged surfaces in the presence of like-charged depletants. A variety of depletants have been used to invoke these forces, such as nanoparticles, micelles, and polyelectrolytes [1-3]. In all cases these structural forces can be well described with an exponentially decaying oscillatory profile and are caused by structuring of the depletants in the solution between the charged surfaces. These phenomena are well described in the literature. However, since both the surfaces and the depletants are charged, double-layer (DL) forces are also present in such systems. Surprisingly, the importance of DL forces in such systems was not investigated so far.

To elucidate the DL forces and interdependence of DL and depletion forces in these systems, we measure the interactions between negatively silica particles in solutions of sodium poly(styrene sulfonate) (PSS) with colloidal probe technique based on atomic force microscope (AFM). The measured force profiles can be decomposed into two parts: long-ranged oscillatory depletion force, and *non-exponential* DL force important at smaller distances. Superposition of DL and depletion forces can accurately describe the measured force profiles, see Fig. 1. Interestingly, the DL interactions in such systems are *non-exponential*, which is atypical for DL forces. However, these interactions can be quantitatively predicted by the mean-field Poisson-Boltzmann (PB) theory. The non-exponential DL profiles are caused by the exclusion of like-charged polyelectrolytes from the vicinity of the surface. This exclusion also defines the DL thickness and the phase of the depletion oscillations, which shows that DL and depletion forces are interdependent. Such description offers a comprehensive picture of the interactions between charged surfaces in the presence of like-charged polyelectrolytes and can be used also the presence of additional monovalent salt [4, 5].

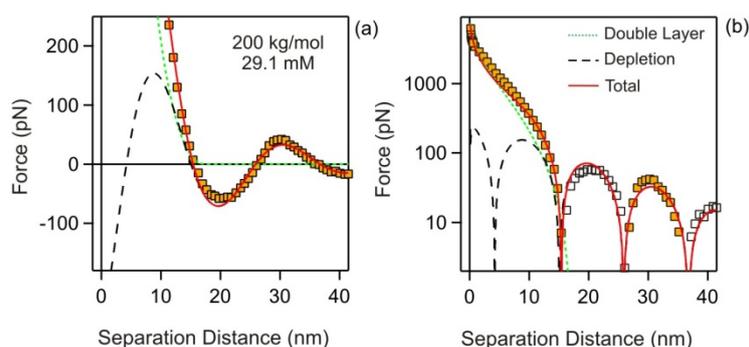


Figure 1: Interaction forces between silica particles in a solution of NaPSS with a monomer concentration of 29.1 mM. Measured data-points are compared with the superposition approximation (solid lines). (a) Linear plot, and (b) semi-logarithmic plot of the magnitude of the force. Depletion and DL contributions are also shown.

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Self-Regulated Ion Permeation through Extraction Membranes and its Control by Ultrasound

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The separation of rare earth compounds from water into an organic phase in practical cases requires the use of specific ion binding ligands in high concentrations. These tend to form complex liquid crystalline phases preferentially at ion rich locations inside a pertraction membrane. They basically form a blocking layer above an ion concentration threshold, which can be experimentally determined. It is manifested in a drastic decrease of the permeation rate, if the ion concentration piles up with time in the pertraction membrane (Figure 1). This in turn inhibits the flux through the membrane, which is studied for the application of rare earth recycling, an example being the phase transfer of Nd from water into organic phase. This feedback leads to a stationary membrane permeation rate that can be modelled without any free parameters in very good agreement with experiment. It is manifested by the constant slope in Figure 1 after a time of 1 hour. The ion specific formation and dissolution of the blocking layer and its control suggest further studies to enhance permeation as well as its selectivity control. The nature of the membrane, responding with lower permeability to an increased concentration gradient is a frequent principle in nature to maintain and control a concentration inside a specific compartment. It is studied here also as regards to structure and viscosity, which is 3 orders of magnitude higher than that of the bulk phases.

In the case a blocking layer can exist, the permeation of the membrane can be enhanced at first by ultrasound but when the blocking layer is formed, the permeation rate decrease to the value without ultrasound. Also if this layer does not exist, the permeation is enhanced by up to a factor of 2 by increasing the diffusivities in the bulk phases involved. The kinetics of ion separation in presence and absence of ultrasound will be modelled, obtaining a quantitative picture of the structures and processes involved

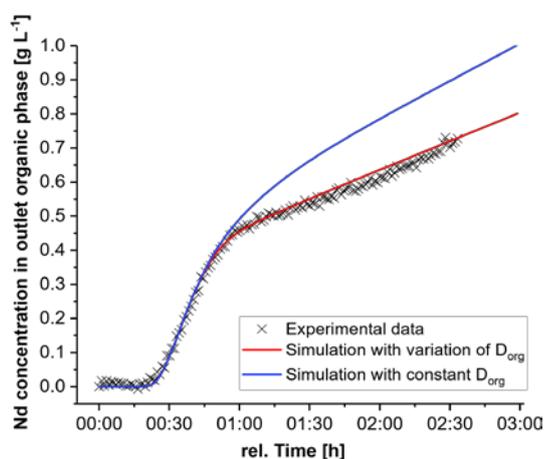


Figure 1. Nd concentration in the oil phase as a function of time after loading the outside of the membrane by a solution of 0.05 M HNO₃ and 1 g L⁻¹ Nd. The organic phase (Isane) contains 0.5 M Bis(2-ethylhexyl) phosphate (HDEHP) as ion complexing ligand. The flow rates are 100 mL h⁻¹ for the water phase and 10 mL h⁻¹ for the organic phase. All simulations with one diffusion coefficient for the organic phase lead to a bell-shaped curve, whereas the measurements with an abrupt slope change can only be simulated assuming a third phase with lower permeability depending drastically on ion concentration. The onset of the establishment of this phase with ion concentration could be verified by bulk experiments.

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Optical imaging of localized chemical events using programmable diamond quantum nanosensors

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Development of multifunctional nanoscale sensors working under physiological conditions enables monitoring of intracellular processes that are important for various biological and medical applications. Nanodiamonds are biocompatible inorganic fluorescent nanoparticles. Their fluorescence that originates from point defects in crystal lattice, for example the so called nitrogen-vacancy (NV) center, exhibit almost no photo bleaching and is therefore observable for unlimited period of time. The fluorescence of NV centers is spin state selective and can be adjusted in a controlled way. This allows to quantify external electric and magnetic fields via optically detected magnetic resonance (ODMR).

We attached paramagnetic Gd³⁺ complexes on the surface of nanodiamonds and created nanoscale sensor of physiological species (pH or redox potential). Gd³⁺ complexes (spin labels) act as a fluctuating magnetic field that can be sensed by NV relaxometry. Nanodiamonds are coated by poly[(2-hydroxypropyl)methacrylamide]-based (HPMA) co-polymer chains. This polymer coating improves nanodiamonds stability, reduce non-specific interaction of proteins and cells and enable further modifications with azide-alkyne cycloaddition catalyzed by Cu(I) ions [1]. Gd³⁺ stable macrocyclic complexes are attached to the surface by either pH- or redox- cleavable linkers. Detachment of Gd³⁺ complexes from nanodiamond surface strongly influences the spin lattice relaxation time T_1 of the NV centers, the more Gd³⁺ complexes on the surface, the shorter T_1 . First, we measured the kinetics of release of Gd³⁺ complexes from the surface upon introduction in different pH or various concentration of glutathione by inductively coupled plasma mass spectrometry (ICP MS). Next, we adopted a single-step method to measure spin relaxation rates enabling time-dependent measurements on changes in pH or redox potential at a submicrometre-length scale in a microfluidic channel that mimics cellular environments. Our sensors operates in a reasonable time scale in a broad range and with high accuracy. Our hybrid nanosensor, owing to its versatility, can serve as a general platform with potential applications ranging from catalytic chemistry to cell biology and physiology, especially for label-free three-dimensional imaging of physiological variables by optical means [2].

Acknowledgements The financial support of the project was provided by Grant Agency of the Czech Republic (Project Number 16-16336S) and Grant agency of Charles University (GAUK project no. 727816).

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Au@Ag@ZIF-8 Nanoparticles as Universal SERS-tags for the robust immobilization of functional proteins

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The use of metal organic frameworks (MOFs) as potential chemical sensors has gaining increasing attention due to large internal surface area, tunable crystal porosity and unique chemical properties of MOFs. More recently, vibrational Raman spectroscopy technique emerged as an alternative to improve sensibility and selectivity in MOFs-based sensors. In this context, metal nanoparticles@MOFs nanocomposites could arise as a powerful platform in biosensing and biodetection due to the combination of the MOFs properties with the SERS (Surface Enhanced Raman Scattering) effect observed on plasmonic surfaces, leading to an improvement in the sensitive in many bio-related. In this study, the encapsulation of Au@Ag nanorods within zeolitic imidazolate frameworks (ZIF-8) encoded with Raman active molecules is demonstrated (see Fig. 1A and 1B). The synthetic strategy is based on the enhanced interaction between ZIF-8 nanocrystals and metal nanoparticle surfaces covered by quaternary ammonium surfactants [1]. Further, surface modification and oriented immobilization of His-tagged proteins were performed based on the interaction of unsaturated Zn²⁺ from ZIF-8 and imidazole moiety of histidines, allowing the subsequent oriented immobilization of functional proteins (see Fig. 1C). Interestingly, the specificity of such interactions allowed the direct purification of His-tagged proteins from a bacterial extract with the Au@Ag@ZIF-8 nanoparticles (see Fig. 1D). The combination of plasmonic properties of the nanoparticles, capable of increasing Raman signal of the different confined dyes, and the direct bioconjugation with His-tagged proteins makes this hybrid system suitable as SERS tags for multiplex detection and imaging in bioapplications.

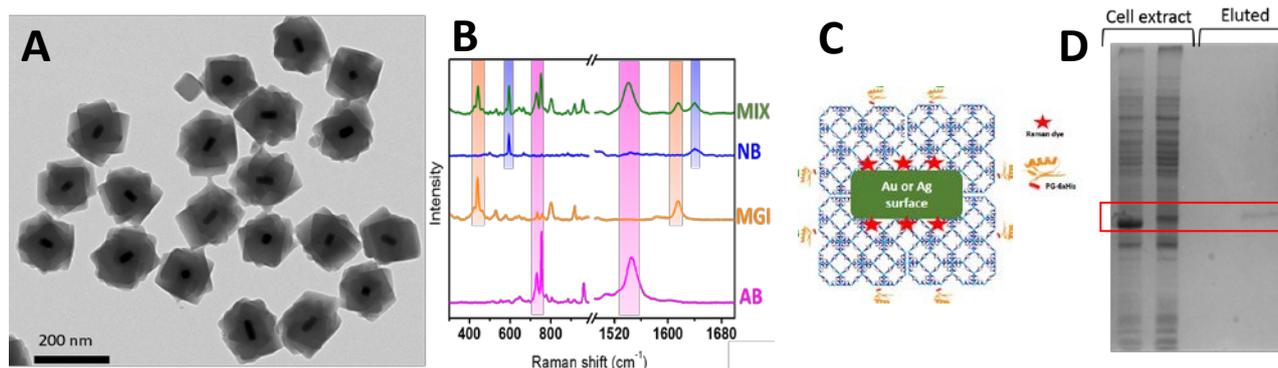


Figure 1 (A) Representative TEM image of Au@Ag@ZIF-8 NPs. (B) SERS characterization of the different encoded particles. (C) Schematic representation of the His-tagged protein immobilization. (D) SDS-PAGE analysis.

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Non-phospholipid-based reverse wormlike micelle formed by a poly(oxybutylene)-poly(oxyethylene) block copolymer

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Contrary to the wormlike micelle formation in aqueous systems, reverse wormlike micelles (RWMs) in nonaqueous solvents have been reported few. In addition, most of RWM systems reported are phosphatidylcholine (PC) based ones [1-3] and non-PC based RWMs are rarely reported [4,5] We report a new non-PC based RWM system by using poly(oxybutylene)-poly(oxyethylene) pentaerythrityl ether (PPE) which has 90 units of oxyethylene and 55 units of oxybutylene (Fig.1).

PPE can be dissolved in isopropyl myristate (IPM) but the solution viscosity was almost unchanged. However, an addition of small amount of water increased the viscosity. Similar behavior was found in other fatty acid alkyl esters but not in aliphatic hydrocarbons. Figure 1 shows the zero-shear viscosity (η_0) values of 10 wt% PPE in IPM with χ wt% water at 25°C. η_0 was almost constant up to 2wt% of water. Then it abruptly increased and reached 56 Pa·s at 2.6wt% of water. With more addition of water, η_0 was decreased. We performed a dynamic rheological measurement on the highly viscous solution and found a viscoelastic behavior which can be fit by the Maxwell model equations. To estimate the micellar structures, we measured conductivity by adding a trace amount of conductive probe, 1-Ethyl-3-methylimidazolium tetrafluoroborate ([emin][BF₄]) which can be solubilized in the interior of reverse micelles. Figure 1 shows that the conductivity is low for non-viscous samples and high for highly viscous samples, suggesting the static percolation caused by RWM formation. The decrease in both η_0 and conductivity beyond those maxima suggests shortening of reverse micelles. We also performed small angle X-ray scattering (SAXS) measurements. SAXS spectra were analyzed by the generalized indirect Fourier transformation (GIFT) method and we obtained pair distance distribution functions, which proved one-dimensional micellar growth as the increase in viscosity.

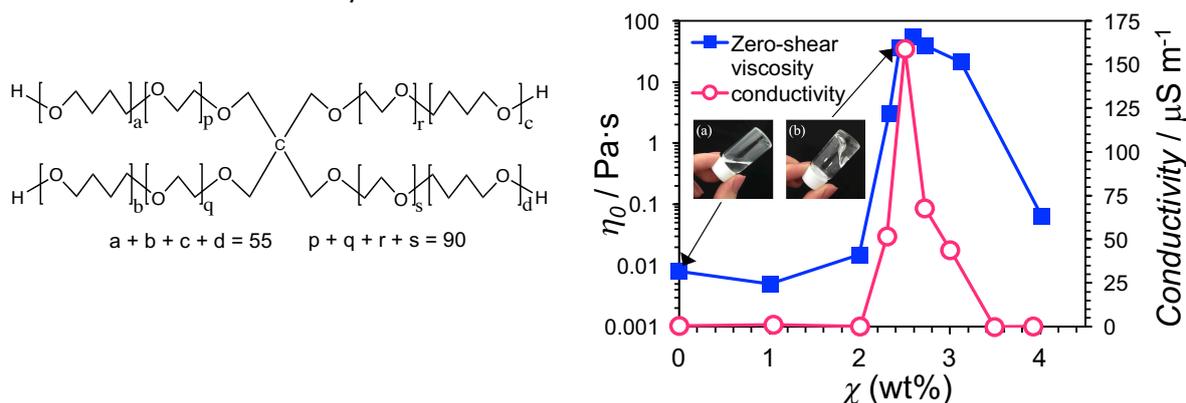


Figure 1 Molecular structure of PPE (left), zero-shear viscosity and conductivity as a function of water content (right)

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Cuboid Phospholipid Vesicles Formed by Template-Free Self-Assembly

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Phospholipid monolayer experiments allow deep insights into the membrane organization at the air/water interface. Combined with bilayer experiments, a complete view of the membrane organization of a particular phospholipid becomes possible. The synthesis of new phospholipids allows us to study the biophysical properties in order to learn more about the forces at play in lipid self-assembly.

Here, we analyze the 1,2-diamidophospholipid Pad-Pad-PC (**1**, see Figure 1). Surprisingly this molecule self-assembles into cuboid phospholipid vesicles [1].

Pad-Pad-PC (**1**) was resynthesized in high purity, optimizing a reported procedure [2]. Then the lipid monolayer was studied under high-brilliance grazing incidence-angle X-ray diffraction at PETRA III (DESY) and the volume systems were analyzed by in house small- and wide-angle X-ray scattering as well as cryo-transmission electron microscopy tomography.

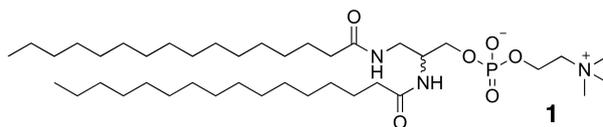


Figure 1 Structure of the 1,2-diamidophospholipid Pad-Pad-PC (**1**).

At low subphase temperature and low surface pressures the lipid monolayer organized in a perfect L'_2 packing at the air/water interface. Upon further compression, the amide-amide hydrogen bonding network was destroyed and a L_2 , O_v , and finally an LS phase was found. In the bilayer experiments a subgel phase was visible. Overall an extremely well packed membrane formed, which showed zero intrinsic and extrinsic curvature, resulting in the formation of non-templated, self-assembled cuboid phospholipid vesicles. Interestingly, the area per lipid chain found in the bilayer (19.2 \AA^2) corresponds to the area found at low monolayer surface pressures of 5-10 mN/m. This suggests that the lateral surface pressure of the bilayer itself is also 5-10 mN/m, contradicting the rule-of-thumb that all bilayers have a surface pressure of approx. 30 mN/m [3].

Acknowledgements The financial support of the Swiss National Science Foundation and the State of Fribourg is acknowledged.

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Transport on Liquid Surfaces by Marangoni Flows

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Gradients in surface excess concentration of surfactants adsorbed to a liquid/liquid interface create surface tension gradients that drive Marangoni flows. Such induced flows have been well studied in the literature. In this talk, we will focus on the ability of the flow to transport various components of the system across the interface.

Initially, we will discuss the case when a single drop of surfactant solution is placed on the surface as the source of the surfactant driving the Marangoni flow. The solution also contains a non-surface active specie, and the solvent in the drop is miscible with the subphase. Inert particles are pre-deposited on the surface and are transported across the surface by the Marangoni flow. We track the transport of each component of the system with time. Next, we will examine the case where the surfactant and non-surface active specie are delivered via an aerosol onto the liquid surface. Here the transport mechanism is not the spreading of individual aerosol droplets, but rather the surface tension gradients that develop between areas of direct aerosol deposition and areas outside that region. The latter two case has direct application in the development of surfactant enhanced transport of pulmonary drug in patients with obstructive lung diseases. *expetendis nec, an duo singulis salutandi explicari, te voluptua evertitur nec* [3].

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Figure 1 Figure legend.

Anti-Icing Surfaces with Low Adhesion to Condensed Microdroplets

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Icing on solid surfaces leads to operational difficulties and high maintenance efforts for power networks, aircraft, ships, ground transportation vehicles and house-hold refrigerators, to name but a few. In extreme cases, icing on surfaces causes disastrous events such as crash of aircrafts and collapse of power networks, which result in severe economic impact and large loss of life. When the supercooling is low, it would be possible to remove supercooled liquid water from the solid surfaces before freezing occurs. To achieve this, we designed and constructed surfaces that show ultralow adhesion to condensed microdroplets; and the condensed microdroplets could be timely removed by self-propelled jumping, which is driven by the released surface energy during the coalescence of microdroplets. The ice formation is delayed and the accumulated ice is decreased greatly on the designed surfaces with ultralow adhesion to condensed water.

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Structural transitions with variation of the secondary fluid volume fraction in liquid-liquid-solid systems

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Ternary liquid-liquid-solid systems exhibit a wide variety of different morphologies depending on the ratio of the three components. With small amounts of secondary fluid, the characteristic mechanical strength of such capillary suspensions arises due to the capillary force inducing a percolating network of particles bridged by small individual droplets of secondary fluid [1]. Spatial information on the structure of such particle networks can be obtained using 3D confocal microscopy on an index-matched model system and directly correlated to changes in the mechanical strength [2]. It was previously shown that the contact angle strongly influences the structure, where the maximum in strength recently had been obtained at a contact angle, which the second fluid forms towards the particles, around 115° when porous particles are used [2]. Using the same particles, we investigate microstructural properties and transitions as the volume ratio of secondary fluid to particles, $\phi_{\text{sec}}/\phi_{\text{solid}}$, is changed from 0.00 to 1.54. Samples with a smaller contact angle of 87°, which forms weaker networks than for 115°, are additionally examined. Example confocal images of some of the newly investigated samples are shown in Fig. 1. These images clearly show a transition from a granular system without added liquid, through a sparser capillary suspension network at intermediate volume ratios, to a network of dense aggregates at larger ratios.

Computational analysis of 3D confocal images provides structural parameters like the coordination number of contacts a particle shares with its adjacent neighbors. The mean coordination number lies around 4 when the particle network is fully established but, due to particle agglomeration, increases when more secondary liquid is added. The position and size of second fluid drops around particle contacts is also evaluated. A change from binary bridges to more complex funicular and clustered arrangements is observed when the volume ratio is increased. These transitions are shifted to higher volume ratios for the sample with 87°, which explains their apparent reduced mechanical strength found in the recent study. Furthermore, the interfacial shape of individual secondary fluid droplets in contact with one or more particles is imaged more closely. Variations of the elastic shear modulus determined from rheology correlate well with the microstructural changes of particle contacts and second fluid volume entities.

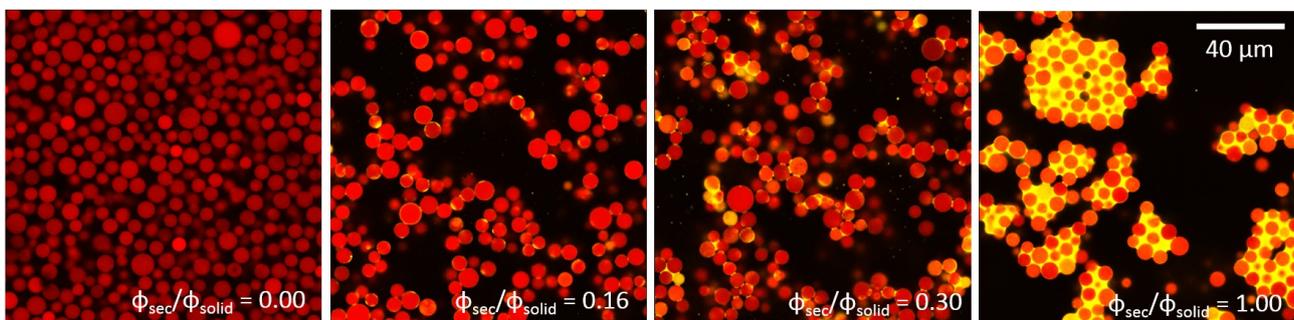


Figure 1 Capillary suspensions based on silica beads (red) with increasing volume fraction of secondary liquid (yellow).

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Rearrangement of lipid lamellar structures under synovial joint-like conditions

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Understanding the tribology mechanisms of articular joints has the potential to facilitate new strategies for counteracting pain due to joint diseases, and to suggest new approaches to decrease energy losses in mechanical devices due to a reduction in friction. Information on the molecular structural organization of biolubricants present in the joint area will provide knowledge on self-assembly relevant to low friction surfaces and thereby facilitate fine-tuning of friction [1]. Lipid molecules, one component of the synovial fluid, form lamellar layers at the cartilage surface and significantly decrease the friction coefficients [2]. The determination of the structure of lipid layers at conditions close to those found in the articular joint during loading (low and high pressure, different shear rates and influence of other molecules or ions) [3] demands highly sensitive and non-destructive structural methods and dedicated sample environment. We applied synchrotron X-ray reflectivity to study rearrangement in dipalmitoylphosphatidylcholine (DPPC) lipid lamellar layer at the solid-liquid interface. We varied the hydrostatic pressure up to 2000 bar and followed the structural variation of DPPC lamellar layer in the presence of hyaluronan and calcium ions at different temperatures. It was determined that both additives separately lead to an increased stability of the solid supported DPPC bilayer against pressure via incorporation into the outer polar part of the lipid lamellar layer [4], and the combined action of hyaluronan and Ca²⁺ ions resulted in structural changes of the outer and inner lipid layers. The alkyl chains of the lipid molecules change conformation from liquid disordered state to gel state by increase in pressure or decrease in temperature. A special feature of the solid supported DPPC layers is a suppression of the ripple state due to the presence of the liquid-solid interface. Hyaluronan and Ca²⁺ ions increase the region of the liquid disordered phase in which a higher self-healing capacity of lipid layers was observed [5]. The addition of other components of synovial fluid (proteins and glycoproteins) into model solution leads to a more delicate structural response to pressure, shear and temperature, which will require advanced experimental approaches.

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Gold nanoparticle strings and rings in lipid nanodiscs and vesicles

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There is a growing interest in applications of gold nanoparticles in nanobiomedicine, both as therapeutic and imaging agents. To ensure long-time circulation and controlled delivery, gold nanoparticles typically require functionalization and/or encapsulation into nanocarriers. Lipid nanocarriers are among the most commonly used in drug delivery and imaging due to their low toxicity and natural biocompatibility. Encapsulation of small gold nanoparticles into lipid nanocarriers results in gold nanoparticle protection and directs nanoparticle self-organization, which can be exploited in imaging applications. Computer simulations can provide valuable insights in this hybrid nanocarrier design, directing experimental research. Using coarse-grained molecular dynamics simulations with a Martini force-field we investigate the interactions between hydrophobically-modified gold nanoparticles and a mixed dipalmitoyl phosphatidylcholine (DPPC) and dihexanoyl phosphatidylcholine (DHPC) lipid nanodisc or vesicle. We found that hydrophobically-modified gold nanoparticles enter a lipid nanodisk from the rim, where more mobile short-tail lipids are located. In the center of the nanodisc long-tail lipids are tightly packed in a liquid-crystalline manner preventing gold nanoparticle diffusion into this area. This results in accumulation of gold nanoparticles along the nanodisc periphery (Figure 1). With a temperature increase the lipid mobility increases allowing nanoparticle diffusion and clustering into strings. Above the melting temperature of lipid liquid crystalline order nanodiscs transform into vesicles leading to further clustering of gold nanoparticles into rings, which can stall the vesiculation process.[1] We will compare the obtained results to experimental data and discuss the implications of our findings for cell imaging using gold-encapsulated lipid carriers.

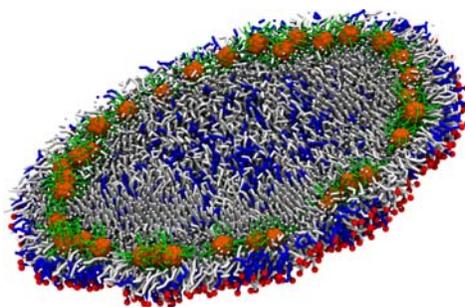


Figure 1. Computer simulation snapshot of a ring of gold nanoparticles along the periphery of lipid nanodisc.

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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 [2,3]. Here we report a novel in-vitro approach for the removal of myeloblasts from peripheral blood samples of acute myeloid leukaemia patients 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 have developed the bioimprinting technology to replicate myeloblasts (AML cells) based on their cell shape and size. Myeloblasts were inactivated with fixatives to preserve the cells 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 the imprint the exposed part of the cell monolayer and was peeled off after curing. Positive replica of the PDMS bioimprint of AML cell monolayers was prepared and the surface pattern was replicated on a large scale by using roll-to-roll printing on PET foil. These bioimprints were surface modified to promote weak adhesion to the myeloblasts which allow them to be trapped selectively on the surface of the bioimprint based on cell shape recognition. We 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 AML cells based on their shape and size (Figure 1). We demonstrate the selectivity of the cell imprints in retention of the cells of matching shape in a mixture with other cells. The removal of myeloblasts from the normal white blood cells based on interaction with a negative bioimprinted surface which selectively attracts and retains myeloblasts. This technology is expected to find application in AML cell separation devices capable of removing myeloblasts from peripheral blood of AML patients which can lead to new blood cancer therapies.

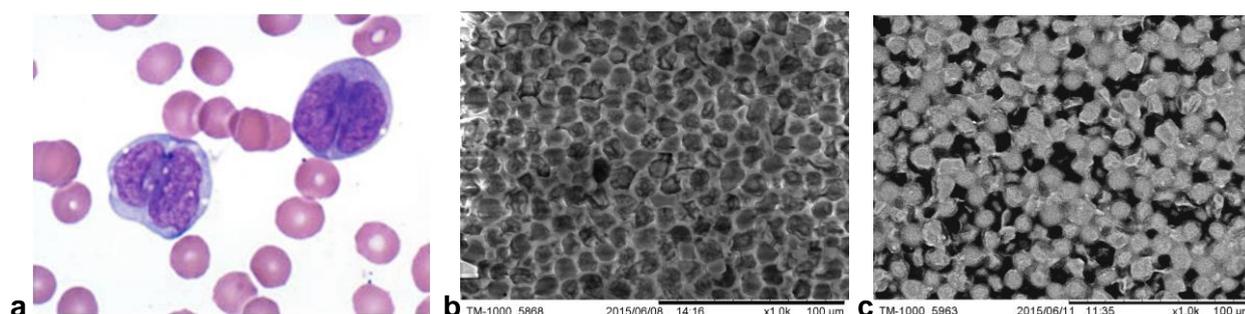


Figure 1. (a) Myeloblasts (AML cancer cells) in a peripheral blood mononuclear cell preparation. Note the difference in shape and size of normal white blood cells and myeloblasts. (b) SEM image of surface of the master negative AML cell multilayer bioimprint on PDMS. (c) SEM image of the surface of a positive AML cell multilayer produced by using a UV curable resin.

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Droplet Transport and Positioning on Smart Slippery Surfaces

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The original focus on superhydrophobic surfaces was due to their ability to create almost complete non-wetting by balling-up droplets of water. Their slipperiness was a by-product of the reduced contact area and contact angle hysteresis. But what if one desires to have World perfectly slippery to water? What are the strategies that can be adopted? And how can smart slippery surfaces be created? The approaches to creating slippery surfaces I will describe all involve removing droplet contact with the solid, whilst still supporting the droplet. The first concept is to decorate the droplet surface with particles, thus creating liquid marbles and converting the droplet-solid contact into a solid-solid contact. The second concept is to use the Leidenfrost effect to instantly vaporize a layer of water, thus creating a film of vapor and converting the droplet-solid contact into vapor-solid contact. The third concept is to infuse oil into the surface, thus creating a layer of oil and converting the droplet-solid contact into a lubricant-solid contact. I will explain how such surfaces can be designed to have smart functionality whilst using the mobility of contact lines and droplets. Our research shows how Leidenfrost levitation can lead to new types of heat engines [1], and how a microsystems approach to the Leidenfrost effect can reduce energy input and lead to a new type of droplet microfluidics [2] (Fig. 1a). We show lubricant impregnated surfaces lead to apparent contact angles [3] and a constant apparent contact angle mode of sessile droplet evaporation [4], and how the large retained footprint of the droplet allows droplet transport and microfluidics using energy coupled *via* a surface acoustic wave (SAW) [5]. We argue that droplets confined between reconfigurable slippery boundaries can be continuously translated in an energy invariant manner [6] (Fig. 1b). We find that a droplet Cheerios effect induced by the menisci arising from structuring the underlying lubricated surface or by droplets in close proximity to each other can be used to guide and position droplets [7] (Fig. 1c). Finally, we show that electric field induced control of droplet spreading, *via* electrowetting or dielectrowetting, can be achieved with little hysteresis [8].

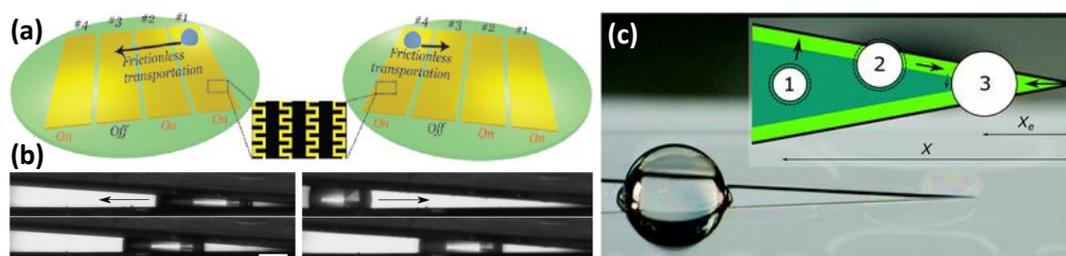


Figure 1 Transportation and positioning of droplets using slippery surfaces: (a) Localized Leidenfrost effect, (b) Reconfigurable boundaries, and (c) Droplet Cheerio's effect.

Acknowledgements The financial support of the UK Engineering & Physical Sciences Research Council (EPSRC) is gratefully acknowledged. Many collaborators at Durham, Edinburgh, Nottingham Trent and Northumbria Universities were instrumental in the work described.

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Spread polyelectrolyte/surfactant films at the air-water interface: effects of aggregate charge and subphase ionic strength

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It has been known for almost one century that spreading amphiphilic macromolecules at the air-water interface allows one to achieve higher surface excesses than the equilibrium layers formed from bulk adsorption¹. Kinetic barriers prevent the trapped network of macromolecules from equilibrating with the bulk. We present an extensive study on the physical properties of kinetically-trapped polyelectrolyte/surfactant films at the air-water interface, which are spread from aqueous dispersion onto an aqueous subphase. The mechanism controlling the film formation is the fast dissociation and Marangoni spreading from liquid crystalline aggregates dropped in a small aliquot onto an aqueous subphase. The interfacial stoichiometry and surface pressure were resolved *in situ* thanks to a new application of neutron reflectometry (NR) that is more accurate and much faster than previous methods². We have found that polyelectrolyte and surfactant molecules bind in a one-to-one molar charge ratio at all the bulk compositions examined, as long as the ionic strength of the subphase is kept low, which is in support of previous predictions³. Surprisingly, the surface excess of both components does not vary significantly over a broad range of concentration of surfactant in the spreading solution. The ionic strength has a more marked effect on the mechanical features of the spread films, i.e. on their stoichiometry and stability studied under dynamic compression/expansion cycles. The different surface behavior and the different stoichiometry when the ionic strength is increased can be explained in terms of loops formation of the polyelectrolyte trapped layer. This work paves the way for the generation of a broad range of ultra-efficient thin films that are prepared from a minimum amount of starting materials. Our novel approach takes explicit advantage of non-equilibrium effects to enhance the interfacial properties of systems that are in common use. We believe that our findings could also have eco-sustainable applications in several technological fields, ranging from coating-based technologies to the production of organic photoactive devices.

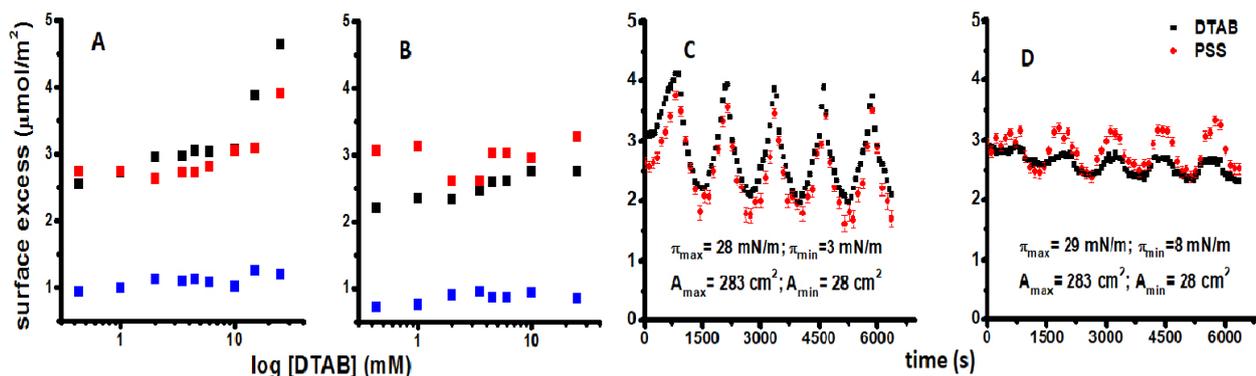


Figure 1 (A and B) Surface excess vs. log [DTAB] in the spreading solution derived from NR onto pure water (A) and 100 mM NaCl (B). The blue squares represent the P/S ratio. (C and D) Dynamic surface excess vs. time onto pure water (C) and 100 mM NaCl (D) during 5 consecutive compression/expansion cycles of the interface. Max and minima represents full compression and full expansion respectively. The corresponding film pressure and area (π and A) are reported below.

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Continuous Isotropic-Nematic Transition in Amyloid Fibril Suspensions Driven by Thermophoresis

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Proteins can form complicated self-assembled structures such as, among others, beta sheets and elongated structures known as amyloid fibrils. In recent studies scientists have related the formation of amyloid fibrils to the Alzheimers disease [1] thus a better understanding of the behaviour of amyloid fibrils has a crucial importance. In the present work we investigate β -Lactoglobulin (BLG), a model protein found in milk, which can be easily harvested and prepared to induce the formation of self-assembled fibrils of different length. We performed a complete study of the thermophoretic behaviour of fluorescently labelled BLG fibrils where we induced a temperature gradient across a microfluidic channel and we monitored the temporal evolution of the concentration gradient over time [2]. BLG fibrils present a negative Soret coefficient, meaning that they tend to accumulate towards the hot side of the channel, over the whole range of average temperature we tested; their average temperature dependence is consistent with the model proposed by Iacopini and Piazza [3]. Because of the aspect ratio of BLG fibrils (in our case, typical size of about 10 μm in length and 4 nm in width), they have characteristics typical of liquid crystals once dispersed in solution. In particular, for concentration higher than about 0.3-0.4% they transition from isotropic to nematic phase [4]. Finally, by fully exploiting the thermophoretic behaviour of BLG fibrils, we were able to induce a continuous isotropic-nematic phase transition in a microfluidic channel by generating a concentration gradient that spanned between approximately 0.2% at the cold side and 1% at the hot side.

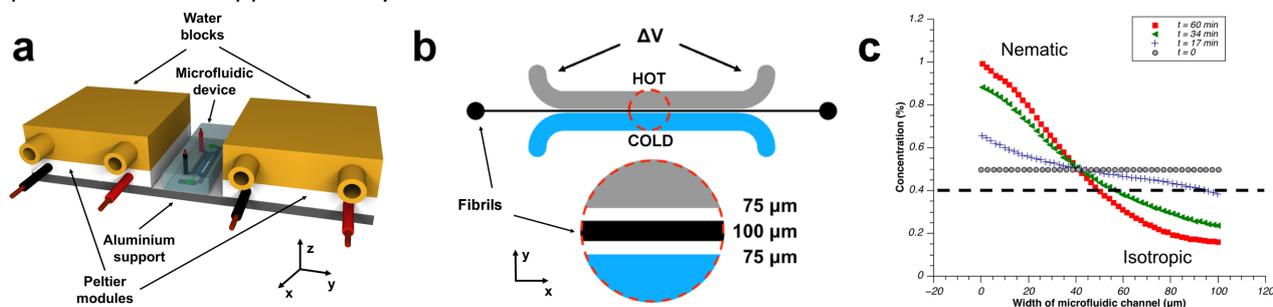


Figure 1 a - Schematic of the experimental setup for thermophoresis. b - Detailed view of the microfluidic channel. c - Temporal evolution of the concentration profile of a 0.5 % w/w sample, at an average temperature of 17.8 °C in the presence of a temperature gradient of 20 °C/mm. Two-dimensional concentration profiles at different times. The black dashed line corresponds to the critical fibril concentration for the I-N phase transition.

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Nanostructuring Biomaterials with Specific Activities towards Digestive Enzymes for Controlled Lipid Hydrolysis

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Understanding and controlling the interaction between triglyceride molecules and digestive enzymes, specifically pancreatic lipase, is of fundamental importance for the rational design of intelligent functional foods and drug formulations.[1] However, the mechanism of lipase action is a complex, interfacial process with significant conjecture in literature regarding parameters that influence catalytic activity. Strategic investigations were performed using advanced surface-sensitive analytical techniques, such as ToF-SIMS, QCM-D and TERS, to analyse the interplay between key material characteristics and lipolysis kinetics. Novel particle-lipid hybrid systems with controlled nanostructures and surface chemistries were fabricated to manipulate the kinetics, disposition and self-assembly structures of digestion products.[2]

Several important factors contributing to enhanced or inhibited lipase activity were identified: (i) the interfacial surface area of lipid modulates the interaction between lipase and the lipid substrate; (ii) a pore size slightly larger than the molecular diameter of lipase is optimal for catalytic activity;[3] (iii) adsorption of lipase molecules to hydrophilic silica surfaces promotes exposure of catalytic domains away from the surface, enhancing lipase-mediated digestion kinetics; while adsorption to hydrophobic surface hindered conformation changes to lipase molecules and retarded lipolysis;[4, 5] and (iv) the interference effect of digestion products was significantly reduced in porous particles where an electrostatic repulsion exists between the negatively charged digestion products and particle surface.[6] These findings can be harnessed to regulate excess fat absorption and energy intake for the improved treatment of obesity, as well as control the enzyme-triggered release of encapsulated bioactive lipophilic molecules (Figure 1).

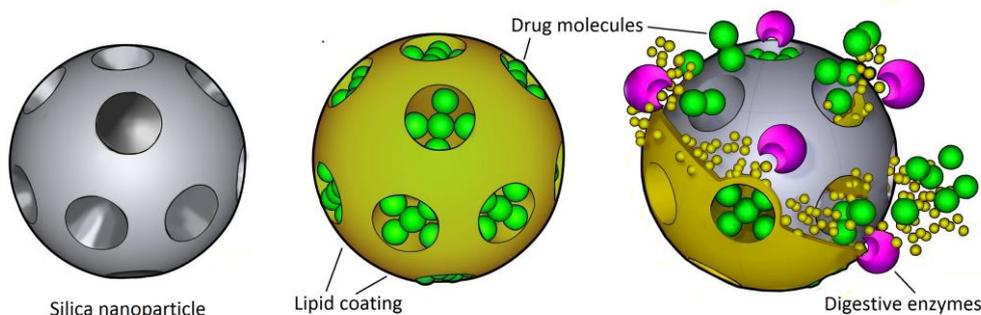


Figure 1 Schematic illustration of silica-lipid hybrid particles for enzyme-mediated release of encapsulated drug molecules.

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Evaporation of liquid droplets

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Liquid drop evaporation is of fundamental importance in many technological processes ranging from heat exchange, ink-jet printing, aerosols, etc. In the simplest case of a spherical cap pure fluid droplet on a flat hard substrate with a relatively small thermal conductivity, three different stages can be identified during evaporation.¹ In the first one the contact angle decreases with time while the radius of the drop base remains constant; in the second stage the contact angle remains constant and radius of the base shrinks; finally in the third stage both variables decrease until the drop disappears. It has been found that for the first and the second stages it is possible to describe the evaporation kinetics according to two universal laws with very good agreement with the experimental results of different liquids on substrates of different hydrophobicity. However, no theoretical description exists for the third phase.

In the case of mixtures of two liquids the situation is more complex. In the case of surfactant solutions it has been found that the first stage follows the universal curve predicted for pure fluids. However, for highly diluted mixtures the second stage of evaporation deviates from the universal behaviour. The deviations were qualitatively explained in terms of the competition between the kinetics of evaporation, of adsorption at both the liquid/air and the liquid/liquid interfaces. However, we have recently found that mixtures of hydrocarbons with different volatilities present deviations even for the first stage of evaporation.

The case of nanosuspensions is of special technical importance and present an additional feature, the so-called "coffee-ring effect".² The deposit formed after complete evaporation frequently does not allow to observe the second stage of evaporation, and leads to a pinning-depinning effect of the three-phase contact line.

Acknowledgments

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Long-range overcharging: Finite concentration colloidal suspensions

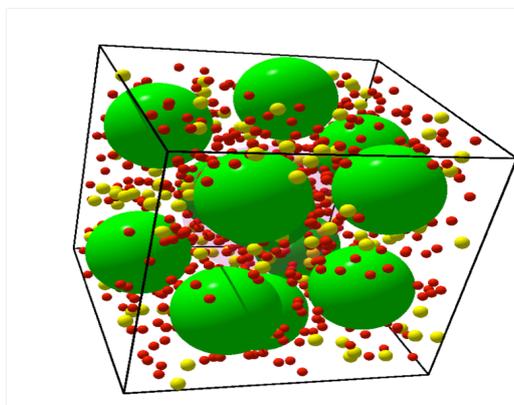
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In the past a new effect of *overcharging*, also referred to as *surface charge amplification*, in finite concentration colloidal dispersions was predicted [1], which has received attention in the literature [2-8]. This overcharging phenomena appears in the very near vicinity of the central macroion, at colloidal infinite dilution. Here we present theoretical integral equations results that predict overcharging far from the central macroion, at colloidal high charge and *finite* volume fraction. We confirm this novel surface charge amplification effect via Monte Carlo simulations.



Snapshot of a Monte Carlo simulation of a model charged, colloidal dispersion (big green spheres), immersed into a 1:1, 0.1M-electrolyte solution. The counterions and coions are the red and yellow little spheres, respectively. Volume fraction=0.24, colloidal particles surface charge=0.1 C/m².

Acknowledgements The authors thank CONACyT financial support through Project No. 169125. E.G.T. acknowledges the support of the Computer Center Technicians of the IFUASLP.

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Elasticity induced force reversal between active spinning particles in dense passive media

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Recently, we have shown that active rotating particles in concentrated passive colloidal suspensions tend to aggregate [1,2]. We developed a synthetic hybrid active-passive system composed of a dense monolayer of passive particles doped with ferromagnetic particles, which were our active agents. Under the actuation of a rotating magnetic field, the ferromagnetic particles spin in place around an axis perpendicular to the monolayer. Using hybrid molecular dynamic simulations of the colloidal particles coupled to a Lattice-Boltzmann fluid, we demonstrated that in the absence of passive particles the interaction between spinners is controlled by secondary flows generated by the inertial contributions of the fluid at finite Reynolds number. In purely active systems, the interactions are governed by this hydrodynamic interaction, and we observed that active co-rotating particles repel each other while active counter-rotating particles attract. In the presence of a passive matrix, the forces acting on the active rotating particles are inverted, resulting in an attraction of co-rotating particles and a repulsion of counter-rotating particles. We showed that the change in the mechanical properties of the matrix from viscous, when suspended in a fluid, to viscoelastic, in the presence of the passive matrix, is responsible for the force reversal. In addition, this change of the mechanical properties of the matrix changes the range of the interaction, so that interaction between active rotating particles embedded in a passive monolayer is extraordinarily increased up to initial distances of more than 16 particle diameters apart. This range of interaction for colloidal soft matter is unheard of.

Apart from this work being the first experimental and theoretical explanation for an attractive interaction between active particles in dense passive media, it has many more potential, far-reaching implications and applications. The interplay between the activity, hydrodynamic interactions, and the mechanical properties of the passive media opens up new possibilities to tune and control these types of interactions. We have also observed that the aggregation process of these active particles produces the annealing of the passive matrix, in agreement with previous observations in similar glassy systems with different types of activity [3]. Therefore, this type of systems may be also relevant from the material processing point of view. In addition, this type of interaction could also be at the core of the mechanism by which active biological molecules can find each other within dense viscoelastic materials such as the highly viscoelastic nucleus of the cell or cell membranes, or at a larger scale it could represent how active cells sense each other in the extracellular polysaccharide matrix. In this sense, activity and elastic work together to overcome the diffusive limitations of such media.

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Liposomal delivery of oligonucleotide therapeutics against antibiotic-resistant bacteria

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Over the last few decades, the overuse and misuse of antibacterial drugs has determined the outbreak of microbial resistance to antibiotics, which represents nowadays a serious global threat [1]. We propose to tackle this issue with innovative oligonucleotide therapeutics based on a dual approach: the nonspecific antimicrobial action of the bolaform cationic surfactant 12-bis-THA is coupled with specifically engineered Transcription Factor Decoys (TFDs) [2] that can block essential genomic targets in bacteria [3,4]. Our efforts are focused on the incorporation of the 12-bis-THA/TFD nanoplexes in fusogenic liposomal carriers by controlling their composition and morphology to optimize the bioavailability and antibacterial activity of drug [5]. The inclusion of the bolaamphiphile in the lipid bilayer and the encapsulation of the oligonucleotide are investigated by means of dynamic light scattering (DLS), Zeta-potential measurements, small-angle X-ray scattering (SAXS), UV-Vis absorption and fluorescence spectroscopy. The antibacterial activity and cytotoxicity of these delivery systems are evaluated with in vitro assays, while confocal microscopy experiments on fluorescently labelled samples allow us to assess the delivery of the TFD into model bacterial systems.

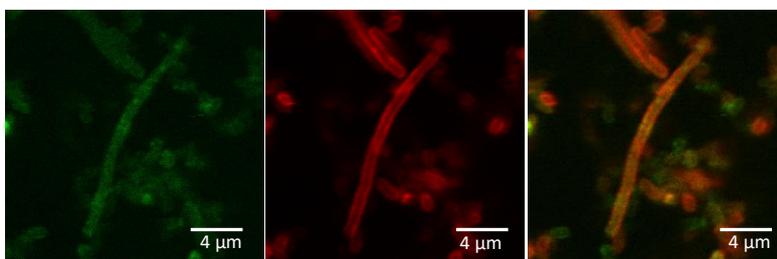


Figure 1 Confocal microscopy images showing the delivery of a fluorescently labelled TFD (green) across *E. coli* cell wall (red) and into the cytoplasm. Left: green channel; middle: red channel; right: overlay.

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Controlled Formation of surface nanodroplets by solvent exchange

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Spontaneous formation of nanodroplets in a ternary mixture is the basis for many processes, from preparation of pharmaceutical products, formulation of cosmetics and insecticides, and to liquid-liquid microextraction. We have shown recently that under controlled flow conditions, namely solvent exchange, nanodroplets can be produced at solid-liquid interfaces [1,2]. During this process, a good solvent for the droplet liquid is exchanged by a poor one, leading to an oversaturation pulse of the droplet liquid and consequently the droplet formation on substrates. In this talk we will optically follow the evolution of growing nanodroplets on micropatterned substrates from droplet diameters of ~100 nm onwards and reveal the morphological and spatial arrangement of the nanodroplets on surface microstructures [3]. We will also attempt to disentangle the effects of concentration gradients from the extrinsic mixing dynamics by spatiotemporally following the nanodroplet formation confined in a quasi-2D geometry. Finally, we will show that those droplets have significant potential for applications in fabrication of functional 3D surface microstructures and nanoextraction of traces of analytes from aqueous solutions in a simple and fast procedure.

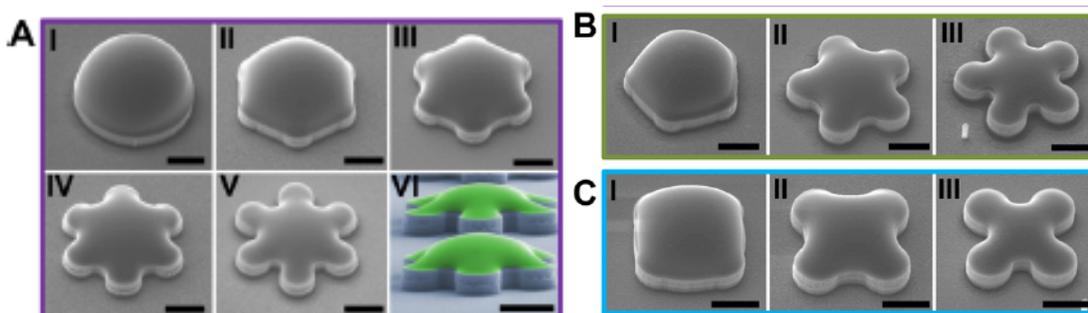


Figure caption: Top-view SEM images of complex micropillars by templating of polymerized dissolving droplets pinned by circular microdomains. Scale bars: 10 μm [3].

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Evaporation of sessile droplets with moving contact lines

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This presentation will summarize some recent progresses in understanding the dynamics of partially or completely wetting sessile drops of volatile liquids, the contact line of which being free to advance by spreading or recede by evaporation. First, as moving contact lines are inherently associated with the well-known divergence of the viscous stress, some theoretical approaches enabling its relaxation are presented, in parallel with the corresponding resolution of the evaporation flux singularity [1,2]. Second, a recent asymptotic theory of evaporating sessile droplets is outlined, focusing on the possibility of reducing the overall dynamics to a simple coupled system of two ODE's for the radius and volume [3].

Then, experimental results (mostly based on Mach-Zehnder interferometry) and interpreting theories are presented about: i) the values of apparent contact angles induced by evaporation, due to intense microflows occurring near the contact line [4]; ii) the effect of buoyancy-induced convection in the gas phase, due to the vapor being heavier than air (here for a pendant droplet, see Fig. 1 – left and Ref. [5]); iii) the influence of the thermal Marangoni effect on the shape of thin droplets evaporating into air (see Fig. 1 – center and Ref. [6]); iv) the competition between spreading and evaporation of droplets deposited on structured substrates (square arrays of cylindrical pillars, see Fig. 1 – right and Ref. [7]).

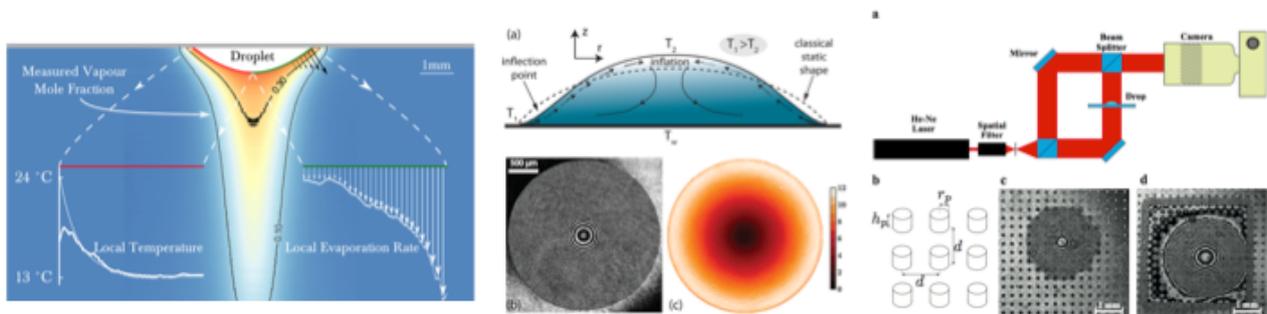


Figure 1 Left: vapor cloud falling from a pendant evaporating droplet. Center: experimental measurements (b,c) and sketch (a) of the shape changes induced by thermocapillarity while a droplet evaporates. Right: sketch of MZ interferometry (a), pillar geometry (b) and typical results (c,d) for droplet spreading/evaporation on pillar arrays.

Finally, if time permits, some recent results will be briefly presented about: i) the Leidenfrost effect; ii) evaporation, spreading and self-emulsification of droplets of binary liquids deposited on a liquid bath; iii) droplet spreading and solidification on cooled solid substrates.

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Structural insights into nanocompartmentalized stimuli responsive microgels by superresolution fluorescence microscopy

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Microgels are cross-linked, swollen polymer networks with sizes in the range of 100 nm to 100 μm . They show properties of both a macromolecule and a colloid. Depending on the monomer composition, microgels can show a stimuli dependent swelling and deswelling, resulting in a change in size of the polymer network. Stimuli can be for example, temperature, pH, solvent composition or redox potential. These special properties offer a wide range of possible applications for microgels. Therefore, high quality analytical tools are necessary to investigate different microgel systems. Common analytical tools to characterize microgel systems are scattering methods, electron microscopy and atomic force microscopy. While scattering techniques only yield information on an ensemble level, microscopy techniques have the potential to give information about the polymer network within single microgels. However, swollen polymer networks show only low contrast in electron microscopy. Furthermore, due to their fuzzy surface, imaging with atomic force microscopy is strongly dependent on the force applied to the polymer network and optical (fluorescence) microscopy is limited by diffraction to about half of the wavelength of visible light.

This restriction can be overcome using superresolution fluorescence microscopy methods. We choose single molecule localization microscopy (SMLM) as our method of choice because of several advantages in analyzing soft matter systems compared to other imaging techniques. Using sophisticated labeling strategies, we visualize different compartments of core-shell microgels. Analysis of the two-dimensional distribution of single molecule localizations within single microgels yielded three-dimensional reconstructions of microgel structures [1].

Analyzing the localization distribution of fluorescent dyes inside single microgels we obtain information about the distribution of functional groups within these microgels [2]. Furthermore, we obtain three-dimensional information about fluorophore localizations by point spread function engineering [3]. This enables us to directly access the internal structure of core-shell microgels.

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Ion-specific effects on micelles reflect interfacial headgroup-counterion pairing and dehydration: a molecular dynamics/chemical trapping study

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After ~130 years and counting, consensus is still absent on the nature of the ion-specific interactions responsible for the Hofmeister series commonly observed in the properties of association colloids and proteins in aqueous solution. We developed a combined molecular dynamics (MD)/chemical trapping (CT) approach to estimate counterion distributions and extent of ion-pairing in the interfacial regions of cationic micelles (CT reaction (**Figure 1A**) and location (**Figure 1B**)). We estimated interfacial molarities of counterions and water and the fractions of headgroup-counterion pairs in micelles of dicationic, 10-2-10 2X, gemini or mono cationic, CTAX, surfactants, with, respectively, three or two Hofmeister counterions, $X^- = Cl^-, Br^-,$ and AcO^- . The measured physical properties of the micelles, e.g., cmc and α , follow the traditional Hofmeister anion order: $Br^- > Cl^- > AcO^-$ —although AcO^- has intriguing amphiphilic properties. Surprisingly, the computed radial distribution functions from the micelle center of mass of the surfactant headgroups and the reactive arenediazonium ion headgroup ($-N_2^+$) are virtually identical (**Figure 1C**). Thus, the shell thickness, ca. 15 Å, and volumes demarked by the gemini and probe headgroups are identical. The counterion and water molarities and fractions of headgroup-counterion pairs within that region were computed from the MD simulations and compared with those obtained by CT. The counterion and water molarities and fractions of interfacial ion-pairs obtained by both methods are qualitatively consistent, follow the Hofmeister order (water molarity orders are the converse of the counterions), and confirm the essential validity of the force fields chosen for the MD simulations and the primary assumptions of the CT method. Our results show that the interfacial region is broader than the micellar core (**Figure 1C**), is a concentrated salt solution, ca. 1-2 M, and is composed of significant fractions of headgroup-counterion pairs, free ions, water, and a mixed hydrocarbon-water layer at the core boundary. The interfacial region's composition should be sensitive to changes in headgroup structure, counterion type and concentration caused by changes in bulk concentrations and changes in interfacial concentrations should influence the balance-of-forces that determine association colloid formation, size and shape.

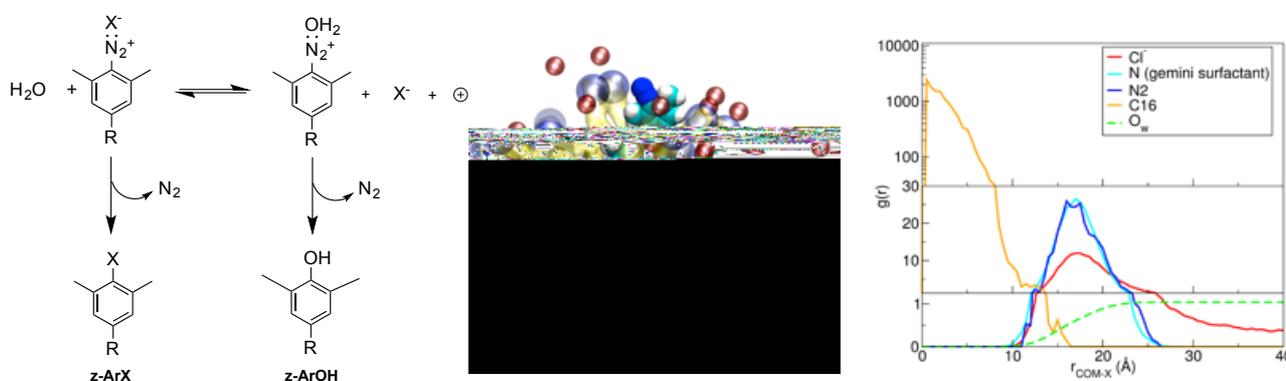


Figure 1. **A** (left) Competitive reaction of the arenediazonium ion probe with X^- and H_2O ; **B** (center) MD simulation of a $C_8H_9-N_2^+$ group and tail of the probe in a gemini micelle; and **C** (right) Superposition of radial distribution functions of probe (dark blue) and gemini (light blue) headgroups by MD.

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New continuous flow chemical reactor for in-situ soft matter research at SANS beamlines

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The past decade has seen many important developments in the field of functional soft matter, from the hierarchical self-assembly of biological systems to polymeric, ‘smart’ materials. The functionality of these systems arises in large part due to their meso- and nanoscale structure which can change dramatically, and often non-linearly, depending on the processing conditions or as a result of external stimuli. The optimisation of such systems and the development of new functional materials therefore relies on the accurate characterisation of the structural changes and their relationship to macroscopic properties. SANS is an ideal method for investigating these complex soft matter systems as it enables selective contrast, avoids beam damage and can be used to investigate materials over many length scales. With the ever increasing flux leading to shorter acquisition times, larger data sets can be acquired, creating an opportunity for the development of sample environments capable of attracting new science and enabling new experiments to be conducted on SANS beamlines.

As part of the development process, we have conceived, assembled and successfully tested an in-situ continuous-flow chemical reactor on the D11 SANS instrument at the ILL, pictured in Figure 1a. The morphological evolution of the micellar aggregates formed in an aqueous solution of a commercial surfactant (RLM 45 CA, structure shown in Figure 1b) with continuously varying pH was studied via sequential additions of basic and acidic solutions. The SANS data, a subset of which can be seen in Figure 1c, not only show the structural changes in unprecedented detail, they also demonstrate the effects of an increasing salt concentration and reveal a previously unobserved effect, whereby the final structures are influenced by the addition rate of the base, exposing a rich, kinetically-driven thermodynamic equilibrium.

Crucially, the experiment has demonstrated the capability of following chemical and self-assembly processes in-situ on a SANS beamline. This is important as it expands the range of techniques available to probe complex soft matter systems and opens the door to a variety of new measurements linking nano- and mesostructural phenomena to macroscopic properties. Our work demonstrates that neutron scattering, coupled with innovative instrumentation, allows us to address and answer interesting questions from self-assembled systems, thereby yielding new insights into the kinetic and thermodynamic conditions that govern them.

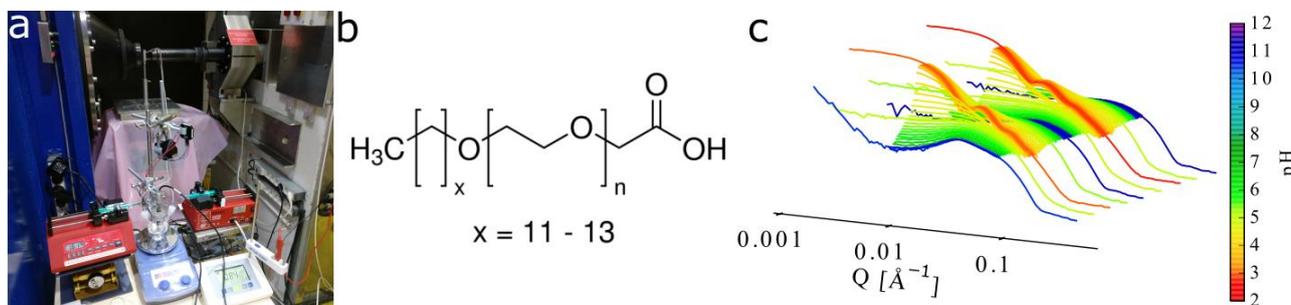


Figure 1 (a) Experimental set-up of the prototype continuous-flow chemical reactor *in operando*, (b) the commercial surfactant AKYPO RLM 45 CA used in the preliminary experiment and (c) SANS data obtained over multiple successive titrations of the surfactant solution with NaOH and HCl.

Optimum formulation relationship to quickly predict a solution in many micro- and macroemulsion applications in surfactant-oil-water systems

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The 1974 oil embargo motivated a huge research and development effort first in the US, then in Europe and worldwide, to formulate surfactant-oil-water systems with know-how instruments as pedagogical as Winsor's R ratio, but with commonplace variables and with much more accuracy than by using the HLB number. Shinoda's PIT approach, limited to polyethoxylated surfactants and temperature scans, was extended to the effect of the main formulation variables found in enhanced oil recovery and other practical cases, e.g. oil nature, aqueous salinity, surfactant and cosurfactant types, temperature and pressure.

The basic studies were first carried out with simple systems containing n-alkanes, NaCl aqueous solutions, well defined ionic and nonionic surfactants, alcohols, and variable temperature and pressure.

Systematic studies based on Winsor original ideas were translated into numerical expressions including 5-6 variables to indicate a very general numerical expression of the surfactant affinity difference (SAD) for the oil and water phases, and its dimensionless equivalent so-called hydrophilic-lipophilic deviation (HLD) [1].

$$\text{HLD} = C_p + k_1 \text{ACN} - k_2 S \text{ (or } \log S) + k_3 f(A) + k_4 (T - T_{\text{ref}})$$

where C_p is the characteristic parameter of the surfactant, ACN the oil alkane carbon number, S the NaCl salinity, $f(A)$ the alcohol effect, and T the temperature. k_i are constant coefficients.

An equal affinity of the surfactant for oil and water occurs when $\text{HLD} = 0$. It was called an optimum formulation, as a physicochemical situation associated with the following general characteristics: low interfacial tension (in particular ultra low as required in enhanced oil recovery), three phase behavior with a bicontinuous microemulsion exhibiting a maximum solubilization of oil and water (as required in formation damage, special cleaning, cosmetics), a minimum macroemulsion stability (as required for crude dehydration and desalting, oil-water separation processes).

When HLD is different from 0, its sign indicates the type of macroemulsion produced by stirring as a corroboration of Bancroft's rule, and its variation from zero is associated with the macroemulsion stability and the trends related to its drop size and viscosity [1]. A continuous change in HLD passing through zero produces an emulsion inversion, and eventually results in spontaneous emulsification.

The large amount of research and development carried out in the past 30 years in different areas, has allowed to use the HLD concept with finely tuned and more explicit variables, in particular with complex surfactants and oil mixtures. HLD systematic use avoids the trial and error methods and extremely reduces the time required to find a solution in many applications dealing with petroleum, foods, cosmeceuticals, paints and other micro/macroemulsions cases.

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