NONELECTROSTATIC INTERACTIONS BETWEEN IONS WITH ANISOTROPIC AB INITIO DYNAMIC POLARISABILITIES

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Ion specific effects are common in colloidal and biological systems. Bubble lifetime before coalescence depends on the electrolyte. The strength of different salts at precipitating proteins leads to Hofmeister series. Theories of ion and colloid interactions based on electrostatics alone, including the Debye-Hückel theory of electrolytes or the DLVO theory of colloids, are unable to predict these ion specific effects. Rather, the theories need to be modified to account for quantum mechanically derived nonelectrostatic dispersion interactions [1].

The dynamic polarisability $\alpha(i\omega)$ of an ion lies at the heart of its dispersion interactions. In general it may be written as a sum over many quantum modes, each with frequency $\omega_n$. Approximations in the past have reduced it to a single mode with modal frequency derived from the ionisation potential (IP) of the ion [2]. We have calculated the exact dynamic polarisabilities of a wide range of ions [3] using ab initio quantum mechanics and present here comparisons against the single mode IP approximation.

The error in calculated dispersion energies due to the single mode IP approximation averages around 40%, and reaches as high as 86% error for halide ions. Ionic self energies, and ion-ion and ion-surface interaction energies are calculated. Applications to activity coefficients in the bulk electrolyte and ion concentration profiles at air-water and oil-water surfaces are presented. Hofmeister series in the activity coefficients of alkali halides consistent with experiment are found.

We also discuss further development of the theory of dispersion interactions with the aim of obtaining a quantitatively, not merely qualitatively, predictive theory. The steps include (i) taking into account the nonspherical anisotropic features of the ions, (ii) using a nonlocal description of the solvent to include solvent spatial structure. Step (i) should be crucial in resolving the adsorption of anisotropic ions such as OH$^-$ to interfaces, which is currently subject of debate between theory and experiment [4].

References:
EFFECT OF ION DISPERSION FORCES ON THE ELECTROKINETIC BEHAVIOUR OF COLLOIDS

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Looking for an explanation for the long-standing issue in colloid science and biophysics of ion specific effects, we include the effect of ionic dispersion forces in the analysis of the colloidal electric double layer. To this end, a primitive model of electrolyte has been simulated including the dispersion interactions given by the Lifshitz theory [1-3]. In this respect, the combined effect of ionic dispersion forces together with the ion size on the electrokinetic behaviour of colloids, is analyzed through Monte Carlo simulations. Our final results suggest that the ionic Van der Waals forces are responsible, to some extent, for the specificity of the zeta potential. Furthermore, we include a preliminary ionic dehydration model that improves the qualitative agreement between experimental data and our simulations considering ionic dispersion forces. In this way we have found in Monte Carlo simulations a predictive tool for ion specificity without considering any phenomenological parameters, a priori unknown.

References:
AMPHIPHILIC FILMS ON BROWNIAN PARTICLES: STRUCTURE, INTERACTIONS AND EFFECTS ON COLLOIDAL STABILITY

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The presence of charged molecules attached on the surface of Brownian particles can dramatically affect their mutual interaction as well as that with foreign surfaces. Therefore, knowledge about how molecules adsorb and assemble on the surface of Brownian particles is required in order to improve functionalization and targeting. We present a study on the relation between the surface states of surfactant molecules on sub-micron particles and the resulting colloidal interactions. To this aim, styrene-acrylate copolymer particles and two different ionic surfactants have been used. Based on a novel methodology recently developed in our lab, the evolution of surfactant layer thickness on colloidal particles can be resolved at nanometer scale, as a function of the surfactant concentration [1]. A phase diagram of the surface states, in terms of the spreading pressure as a function of the molecular area, is obtained from the adsorption isotherms. The results indicate that an initial, gas-like state of noninteracting adsorbed molecules is followed, with increasing surfactant concentration, by condensed domains or hemimicelles prior to reaching full coverage of the particle surface. Seeking an independent validation of this model by other means is difficult. For example, surface imaging techniques (e.g., AFM) are not well-suited to this aim, given the intense Brownian motion of the particles. Therefore, a novel protocol has been devised by which the system, at varying surfactant concentration, is sheared at very high shear-rate in a microchannel and the extent of aggregation is quantified by small-angle light scattering. With no added salt, it is shown that the surfactant films on two particles can fuse/adhere leading to aggregation as long as an even small-sized uncovered polymer patch is present. In the opposite case of fully developed films, by analyzing the mechanism of shear aggregation in the low-salt limit theoretically, we show that, whenever hydrophobic patches are completely absent, short-range hydration repulsive forces dominate over DLVO forces and adhesion/aggregation can never be achieved even upon application of extremely high collision energies. Consistently, a lower-limiting boundary for the hydration interaction is calculated [2].

References:
DEPLETION-DRIVEN AGGREGATION KINETICS OF OLIGO (ETHYLENE GLYCOL) COATED GOLD NANO PARTICLES WITH PROTEIN IN SOLUTION

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Self-assembled monolayers (SAM) with oligo(ethylene glycol) (OEG) termination are of great importance in biomedical applications due to their protein resistance property. We have successfully prepared OEG-SAM decorated gold nanoparticles and studied various interactions, stability and aggregation kinetics of colloid in the mixtures with protein by real-time SAXS and UV-vis spectroscopy [1-3]. Adding protein to SAM-coated colloidal gold solutions results in an attractive interaction between colloids which has an origin of depletion effect. Above a critical concentration, c*, the colloids lose their stability and form aggregates [2]. Real-time SAXS results on the aggregation process indicate that the structure of the aggregates is amorphous clusters. The depletion-driven aggregation kinetics was studied by UV-vis spectroscopy under various protein concentrations, ionic strength and type of salts. At low salt addition, a kinetic crossover from RLCA to DLCA was observed, which is caused by the effective repulsive interaction barrier between colloids within the oscillatory depletion potential. Above 0.5 M NaCl, the surface charge of proteins is screened significantly, and the energy barrier disappears, thus the growth kinetics becomes DLCA only [3]. The stability of the SAM-coated colloid and colloid-protein mixtures also depends on the nature of added salts. The colloid solution was found to be stable in the presence of NaCl, NaSCN, MgCl₂, but lose its stability with Na₂SO₄ above 0.3 M. In the mixtures with protein concentration close to c*, addition of NaCl or Na₂SO₄ enhances the colloid aggregation, NaSCN tends to stabilize the solution, MgCl₂ leads to a long induction time before aggregation. The observed salt nature effects follow the “Hofmeister series” and have been discussed based on the salting-in or salting-out effect as well as the ion-absorption effect [4].

References:
COMPETITION OF PHASE SEPARATION AND KINETIC ARREST IN A BINARY MIXTURE WITH DEPLETION ATTRACTION

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The behavior of highly concentrated colloidal dispersions is a topic of current interest with respect to practical applications as well as for the fundamental understanding of soft condensed matter. Recently it has been shown that the introduction of short-range attractions by the addition of free polymer leads to such effects like melting of a colloidal glass and appearance of a reentrant glass transition \cite{1} connected with the existence of a new glassy state at high polymer concentrations - the ‘attractive’ glass. Besides the change of the dynamics on introduction of the depletion, there are various scenarios of the phase separation depending on the colloid volume fraction and the attraction strength.

The studied colloidal system consists of a binary colloidal mixture of 1:50 cross-linked polystyrene microgel particles in a good solvent. To introduce short-range attraction various amounts of linear polystyrene were added. A binary mixture was chosen to suppress crystallization and the size ratio \( R_{\text{g,polymer}}/R_{\text{colloid}} \sim 0.08 \) should exclude a fluid-fluid phase separation. Nevertheless, when driving the system into the attractive glass, a pronounced waiting time dependence of both density fluctuations (measured by DLS) and mechanical properties (as seen by bulk rheology) was observed. We used time resolved SLS to check whether this waiting time dependence is due to aging or it is connected to structural changes. We found evidence that this behavior is due to a micro phase separation of A and B particles with the concomitant formation of pure crystalline A and crystalline B micro domains. This phenomenon is reminiscent of the fractionation of polydisperse emulsion droplets via depletion attraction \cite{2}.

References:
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OTHOKİNETİC HETEROAGGREGATİON: EFFECT OF PARTICLE SIZE RATİO ON AGGREGATE PROPERTİES

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Three different aggregation methods were employed in this work: the addition of HMW polymer, the addition of silica particles (4.3, 105 and 285 nm diam.) and adjustment of suspension pH to 9. Stable alumina dispersions (310 nm) were flocculated using these three methods and each method was found to aggregate the alumina causing equilibrium between formation and destruction of aggregates. The equilibrium size of the aggregates (from largest to smallest) was found to follow the order: HMW Polymer, MP3040, STZL, STXS (285 nm, 105 nm, 4.3 nm) and pH 9. The use of light scattering simulations showed the effect of a second particle species (silica) on the scattering intensity versus wave vector relationship (I versus Q). It was still feasible to obtain a fractal relationship from the light scattering data, even with the complications arising from a two particle asymmetrical system. The fractal dimension increased slightly (2.04, 2.06, 2.19) with an increase in particle size ratio (0.014, 0.339, 0.92) suggesting stronger particle interactions between particles of similar size. The strength of the aggregates was rated from strongest to weakest: HMW Polymer, 285 nm, 105 nm, 4.3 nm and pH 9. HHF calculations where consistent with these results for the three heteroparticle systems. The particle-particle interaction energy was found to be weaker the smaller the silica particles become.
CLUSTER COMPOSITION IN HETEROAGGREGATION OF BINARY MIXTURES

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As aggregation processes become ever more complex in their applications, the interaction of particles with different surface composition, charge or size becomes increasingly important. In the presented study, cluster discrimination was extended from pure cluster size measurement by single-cluster light scattering (SCLS) [1] to the dynamical determination of cluster composition of heteroaggregates in binary particle mixtures by flow cytometry with one particle population being fluorescently labelled. Experiments with oppositely charged polystyrene particles (PS, 2µm, -60mV) and Rhodamine-B labelled melamine-formaldehyde particles (MF-RhB, 366nm, +42mV), were conducted at different concentrations, particle ratios, temperatures and salinities. Furthermore, heteroaggregation in stirred systems was successfully recorded. Due to the size difference and opposite surface charge of both particle populations, PS particles were coated by MF-RhB particles inducing aggregation of destabilised PS monomers. As expected for diffusive systems, aggregation kinetics are enhanced with increasing particle concentration and temperature as well as by stirring. Heteroaggregation is confined to intermediate PS:MF-RhB ratios. At low MF-RhB concentrations PS particles do not aggregate in pure water due to insufficient electrostatic destabilisation, and at very high concentrations aggregation is terminated by restabilisation. De- and restabilisation during heteroaggregation were verified by ζ-potential measurements. Aggregation kinetics were greatly retarded by increasing the electrolyte concentration over several orders of magnitude, showing that particles with attractive electrostatic interparticle forces aggregate quicker than purely diffusive systems.

References:
EVIDENCE AND RELEVANCE OF A STRUCTURAL BARRIER FOR COALESCENCE OF SOFT SPHERE COLLOIDS

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Coalescence phenomena are widely known for heterogeneous systems with liquid-gas and liquid-liquid interfaces. Coalescence of particles is much less intuitive but occurs for elastomer colloids under certain conditions. As for bubbles or droplets, coalescence of elastomer particles depends in general on bulk viscosity and surface tension (surface energy) as driving force. Thus, prerequisite for coalescence is high polymer chain mobility as can be found for elastomer materials at temperatures sufficiently above so called glass transition temperature. In cases of very fast extrusion or immediate coalescence, drainage of liquid film between approaching surfaces and rupture of the liquid film will control the coalescence event. Our investigations aim at contributing to the fundamental understanding of elastomer particle coalescence on the basis of aggregation studies of soft elastomer particles.

Coalescence of elastomer particles can be induced by destabilization of the colloid. Modeling of the aggregation kinetics allows determination of the cluster structure where fractal structure is indicated by a low fractal dimension of i.e. 1.7 to 1.8 for diffusion limited aggregation and full coalescence by a fractal dimension of 3.0. Both situations have been found for elastomer latex of the same polymeric material but different surface characteristics. At 25°C anionic surfactant stabilized particles always coalesce, forming spherical clusters. Particles carrying fixed polar surface groups in contrast form fractal clusters upon aggregation. The coalescence behavior of the first particle type indicates no limitation with respect to flow ability of bulk material. Since both latexes are of identical bulk material, drainage and rupture of the separating liquid film are assumed to control the coalescence process. Intuitively, one may expect that any physicochemical parameters that reduce the mobility of water molecules in the contact region would restrict coalescence. On the other hand, it is known [1,2] that any ionic species can affect the water structure at interface. Then, polar surface groups or cationic surfactants at the solid-liquid interface may raise a structural barrier between interacting particles. Such a non-DLVO, short range repulsive interaction is often referred to as hydration interaction. Although understanding of the complex phenomenon ‘hydration barrier’ is far from complete [1] it is generally accepted that an increase in thermal energy is associated with easier dehydration of ionic surface groups or counter ions respectively a reduced order or smaller extension of hydration layer at the particle surface. In this way the structural barrier between attractive particles should be reduced. Indeed, we find full coalescence for the particles with fixed polar surface groups above a certain temperature, which might indicate the collapse or sufficient reduction of the structural barrier. Coalescence of the surfactant stabilized latex already at ambient temperature is explained by the mobility of surfactants that might get squeezed out of the interaction gap readily when particles approach.

References:
UNDERSTANDING THE SURPRISES OF DNA-MEDIATED COLLOIDAL INTERACTIONS

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Self-assembly of nano-microscale particles is a powerful way to obtain new materials, provided that one has good control over the particle interactions. One approach is to coat particles with complementary, single-stranded DNA ‘sticky ends’, which give rise to highly selective, thermo-reversible attractions. However, despite considerable experimental and theoretical work, most successes at assembling specific structures are still largely based on trial-and-error.

To acquire a better understanding of DNA-mediated interactions, we investigated the aggregation and dissociation behavior of micrometer-sized colloids as a function of the temperature, the sticky end coverage and the type of DNA construct. We found that the particles display surprisingly sharp dissociation transitions, which can only be explained if DNA-mediated repulsive entropic interactions are taken into account, besides the hybridization-mediated attraction. We have developed a simple quantitative model for these interactions, based on the measurable properties of the elementary constituents: the melting curves of the complementary sticky ends in solution, the length of the spacers between the particle surface and the sticky ends, and the surface coverage. With this model we demonstrate fine control over the dissociation temperature and the sharpness of the dissociation curve, both essential properties for complex self-assembly processes.

In a second line of investigation, we studied the aggregation behavior of colloids coated with self-complementary ‘palindrome’ sequences, as these are particularly useful for certain applications. Unlike ‘normal’ Watson-Crick sticky ends, we found that it is of great importance whether the palindrome sticky end is attached to a flexible single strand or a rigid double-stranded ‘rod’. While the latter system displayed normal dissociation at elevated temperature, the former system showed enhanced aggregation with increasing temperature and no aggregation during fast temperature quenches. We can quantitatively explain these surprising observations by a competition between intra- and interparticle bonds. This provides us with an additional level of control over the interparticle bonding and greatly facilitates the formation of self-assembled finite-size structures.
ASSEMBLY KINETICS IN BINARY MIXTURES OF PATCHY COLLOIDS

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Assembly of particles forming composites with different shapes and functionalities is of great interest for material and biological scientists [1].

We investigate the self-assembly kinetics [2] of bi-disperse beads: streptavidin-coated polystyrene beads (A) with diameter 1 µm and biotin-coated polystyrene beads (B) with diameter 0.150 µm. The biological specific attraction [3] leads to two distinct aggregation kinetics: (i) the linkage of the two kinds (large-A and small-B) of colloids; (ii) the assembly of the large beads once the small ones are attached, through the patchy B-spots.

We study both kinds of aggregation kinetics in dependence of the A-B spheres number ratio (N) by performing Dynamic Light Scattering that allows us to distinguish the dynamics and the relative amount of the different components in the described poly-disperse system. The different formation and growing of aggregates during the waiting time in relation to the number of bonds is clearly shown. Moreover by analyzing the aggregation dynamics at short times using the Smoluchowsky coagulation theory we estimate the two bonding rates of A-B and A-A assemblages. Interestingly both constants have a maximum in correspondence of N\approx 80, signalling fastest aggregation.

In our knowledge the kinetics of “patches formation” together with the rate of the early assemblage (dimerization) of patchy colloids [4] have not yet been exploited.

References:
COOPERATIVE MAGNETOPHORESIS OF SUPERPARAMAGNETIC COLLOIDS: THEORY AND EXPERIMENTS

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An essential step in the development of scientific and clinical applications of magnetic carriers is the control of particle behaviour. Control of particle trajectory in drug delivery applications or extraction from dispersion in immunoassay applications using externally applied magnetic gradients are typical examples. However, the magnetic gradients required to produce a significant magnetophoretic drift in a magnetic carrier are very high, even in the case of superparamagnetic particles. For example, gradients of the order of 10^4 T/m could be found in typical separation columns using a packed bed of magnetically susceptible wires (diameter 50 mm) placed inside an electromagnet.

Here, we present new experimental and theoretical results showing that low gradient magnetic separation (LGMS) is also possible. The key step in this LGMS process is the reversible aggregation of magnetic carriers induced by the magnetic field. We report fast separation (a few minutes for a 25 mL sample) of dispersions of superparamagnetic particles with different concentrations (0.01 g/L to 10 g/L) using a 30 T/m magnetic gradient (the employed particles are commercial Estapor(R) superparamagnetic microspheres and the magnetic separator is commercially available from Sepmag Tecnologies). The interplay between the different factors determining low gradient magnetophoresis (magnetization of particles, size, is consistently described by a magnetic analogous to the Bjerrum length concept [1]. We formulate a simple criterion predicting the onset of low gradient magnetophoresis separation as a function of the sample properties (e.g., minimum particle radius). The separation times of samples with different concentrations and different particles can be described with a unique curve depending on the ratio between the magnetic Bjerrum length and the particle separation (depending on concentration).

References:
STRONG REPULSIVE INTERACTIONS IN POLYELECTROLYTE-LIPOSOme CLUSTERS CLOSE TO THE ISOELECTRIC POINT: A SIGN OF AN ARRESTED STATE

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Charged colloidal particles whose interacting potential is governed by short-range attraction and long-range screened electrostatic repulsion contributions form aggregates whose shape, size, and overall charge are sensitively dependent on the balance between attraction and repulsion. In some cases, this class of colloidal systems shows an equilibrium cluster phase, where particles associate and dissociate reversibly into clusters.

Our investigation focuses on the aggregation processes which take place in a particular class of colloids, i.e. suspensions of unilamellar charged lipid vesicles (liposomes) and oppositely charged polyions. In this system, an important issue is that the combination of long range electrostatic repulsion and short-range attraction can give rise to the formation of an equilibrium cluster phase, where particles, close to the isoelectric point, form large aggregates, whose size can be appropriately tuned by varying the polyion-liposome concentration ratio (re-entrant condensation). The observed phenomenology suggests that these systems belong to the class of colloids characterized by long-range electrostatic repulsions and short-range attractions, but with a distinctive tract that, in this case, both the repulsion and the attraction share a similar electrostatic nature. In previous investigations, the phenomenology of re-entrant condensation was investigated and it was well stated that the mechanism inducing aggregation is the like-charge attraction between polyion-decorated liposomes (pd-liposomes), due to electrostatic correlations [1].

In this communication, we present some experimental evidences that also the dynamics of the cluster phase is, in the vicinity of the isoelectric point, dominated by the strong repulsions between the aggregates, possibly yielding to an arrested state [2]. By means of combined static and dynamic light scattering and electrophoretic mobility measurements, we have characterized the cluster-cluster interactions between pd-liposome aggregates in the polyion concentration region across the isoelectric point, both in the presence and in the absence of the simple added salt (NaCl). We have observed the occurrence of strong repulsive interactions between these aggregates that may represent the prerequisite for the appearance, also in this particular system, of an arrested state. We propose for this system a justification of the metastable phase, based on a recent model developed by Velegol and Thwar [3] in order to describe the effect of a non-uniform surface charge in the colloidal interactions.

References:
CATANIONIC VESICLES FROM AMINO ACID-BASED SURFACTANTS: CHAIN SYMMETRY EFFECTS

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Catanionic vesicles, besides their natural fundamental interest, currently stand as an interesting alternative to conventional lipid-based vesicles, for which both chemical and long-term colloidal stability can be serious issues. Further use of amino acids for the synthesis of vesicle-forming surfactants enhances the biocompatibility levels needed for a viable alternative to the lipid systems.

In this work, the formation and characterization of catanionic vesicles by lysine- and serine-derived surfactants, synthesized in our team, have been investigated by cryo-TEM and PFG-NMR diffusometry. The lysine-derived surfactant is a double-chained anionic amphiphile bearing a pseudo-gemini configuration, while the serine-derived amphiphile is cationic and single-chained. Vesicles form in the cationic-rich side, for narrow mixing ratios of the two amphiphiles. Further increase of the single-chain surfactant fraction in the mixture causes disruption of the vesicles and formation of micelles. Two pair systems were studied, one symmetric with C12/C12 chains and one asymmetric, with C8/C16 chains (where the Ser-based surfactant has the longest chain). Different mechanisms of the vesicle-to-micelle transition were found, one involving phase separation (C12/C12) and another one with continuous transition with intermediate elongated micelles (C8/C16). The results are interpreted on the basis of currently available models for the the micelle-vesicle transitions and the stabilization of catanionic vesicles (curvature energy vs mixing entropy).

References:
SURFACE FRACTALS IN COLLOIDAL AGGREGATION

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We report, on the basis of static light scattering (SLS) measurements, what we believe to be the first observation of a transition from surface fractal to mass fractal structures in a suspension of aggregating vesicles [1-3]. This morphological evolution is controlled by the amount of Magnesium present in the suspension. Our experiments show that this fractal transition stops at a final stable value of the mass fractal dimension corresponding to very dense structures. These results are in clear contrast with those obtained for another archetypal divalent cation, Calcium. In that case, a DLCA regime, with the classical ramified structures, was detailed [4]. Our light scattering experiments were implemented by means of a cross-correlation scheme [5] in order to clarify the incidence of the multiple intracluster scattering. From infrared spectroscopy analysis, we also conclude that the different dehydration of the lipid membranes exerted by calcium or magnesium plays an essential role in the short-range intervesicles interaction and conditions the resulting cluster morphology.

References:
KINETIC ARREST IN POLYION INDUCED INHOMOGENEOUSLY CHARGED COLLOIDAL PARTICLE AGGREGATION

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Polyions adsorbed onto oppositely spherical charged colloidal particles can significantly modify particle-particle interactions. For sufficient amounts of added polymers, the original electrostatic repulsion can even turn into an effective attraction and relatively large kinetically stable aggregates can form [1,2]. The attractive interaction between two oppositely particles arises from the correlated adsorption of polyions at the oppositely charged particle surface, resulting in a non-homogeneous surface charge distribution. We investigate the aggregation kinetics of polyion-induced colloidal complexes through Monte Carlo simulation, the effect of charge anisotropy being taken into account by a DLVO-like intra-particle potential, as recently proposed by Velegol and Thwar [Langmuir, 17, 2001]. The results reveal that, in the presence of charge heterogeneity, the aggregation process slows down, due to the progressive increase of the potential barrier height upon clustering. Within this framework, the experimentally observed cluster phases [3] in polyelectrolyte-liposome solutions should be considered as a kinetic arrested state. Simulations [2] show that cluster size distributions are strictly dependent on electrostatic parameters describing colloidal dispersions characterized by various polyion/liposome molar ratio. With the increase of the net charge on spherical vesicles or with the decrease of the variance of potential at the particle surfaces, distributions are more peaked around lower value of mean cluster radius and show a characteristic tail compatible with an exponential distribution. For highly electrostatic coupled systems, the use of Velegol and Thwar potential offers an interesting promise for the understanding of the role of the electrostatic attractive and repulsive interactions between charged colloidal particles and oppositely charged polyions.

References:
Dispersions of lipid nanoparticles stabilized by dimyristoylphosphatidylcholine (DMPC) and co-emulsifiers like sodium-glycocholate (SGC) are used for drug delivery. It has been shown that i. a. drug release rate and storage stability depend highly on the properties of the stabilizer [1-3]. Structural differences between mono- and bilayers are known from nanosuspensions of tripalmitin in water [4], where the monolayer is thinner and the peaks of the electron density profile are less pronounced than what one would expect from the structure of bilayers.

Our aim is to investigate the difference in dynamics of monolayers compared to bilayers and the influence of SGC with the long-term goal of linking microscopic dynamics with macroscopic properties like storage stability.

The picosecond-dynamics of DMPC in dispersions of vesicles (diameter ≈ 130 nm) and in stabilizing monolayers of an aqueous hexadecane emulsion was measured at the neutron time-of-flight spectrometer TOFTOF at the FRM II. Using neutron scattering, it is possible to mask hexadecane and water by deuteration. As can be seen in the figures below, it was found:

1. The spectral broadening caused by DMPC in monolayers has a dip at the position of the structure factor maximum of hexadecane, indicating an influence of the molecular structure of the dispersed phase on the mobility of the stabilizer.

2. Pure Fickean diffusion would result in a linear dependence of the spectral half widths HWHM against the squared momentum transfer $Q^2$ which is not observed. A «jump model» fits the data very well.

3. Addition of the co-emulsifier SGC increases the jump frequency whereas the diffusion coefficient seems to be basically unaffected.

Fig. 1. Left: Neutron scattering spectra of DMPC in bilayers at two values of the momentum transfer $Q$ along with the instrumental resolution. Right: Half widths of the broadening versus $Q^2$ with the fit of a jump model.

References:
CONDUCTIVITY OF POROUS PARTICLE SUSPENSIONS

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The conductivity of a suspension of porous or non porous particles depends on three main factors: the electrolyte conductivity, the surface conductivity and the topology of the system. When experiments are done at very high ionic streng th, double layer effects may be neglected and the suspension conductivity depends only on that of the electrolyte and on the topology of the system. It is then useful to define a parameter, called tortuosity, by the following equation
\[ \tau = \frac{\sigma^0 \varepsilon}{\sigma_{\text{eff}}} \]
where \( \sigma_{\text{eff}} \) is the conductivity of the suspension or of a bed of particles, \( \sigma^0 \) is the conductivity of the electrolyte and \( \varepsilon \) the porosity of the system. The tortuosity thus defined is formally similar to the definition based on diffusion coefficients, which are measurable for example by NMR. The tortuosity should depend only on the system topology. Even in the simplest case of a suspension of non porous spherical particles, there is to our knowledge no model able to fit the experimental data of the tortuosity of a suspension in the whole porosity range. Only empirical expressions have been proposed to fit the experimental tortuosity values, such as :
\[ \tau = 1 + p \ln(1/\varepsilon) \]
where \( p \) is a parameter that depends on the shape of non porous particles and their mean orientation in the bed [1]. We verified this equation by conductivity measurements as well as by random walk numerical simulations. A new method is then proposed that allows the discrimination between the contributions of inter-particle and intra-particle porosities to the tortuosity [2]. The intra-particle tortuosity can be derived from the particle conductivity calculated from the Maxwell equation extrapolated at infinite dilution of particles. Ongoing work is done to apply the same concepts to surface conductivity by measuring conductivity of porous particles suspensions at low ionic strength. By using high surface area porous particles, the surface conductivity contribution is considerably enhanced.

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References:
NEW APPROACHES İN DNA-GEL PARTICLES

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Aqueous mixtures of oppositely charged polyelectrolytes undergo associative phase separation, resulting in coacervation, gelation or precipitation. This phenomenon has been exploited here to form DNA gel particles by interfacial diffusion. We report the formation of DNA gel particles by mixing solutions of DNA(dsDNA) with solutions of cationic surfactant (CTAB) or solutions of proteins (either pure lysozyme and pure protamine or mixtures of them). Under optimal conditions, droplets from DNA solutions instantaneously gellet into discrete particles upon contact with the corresponding surfactant or protein solutions (Figure 1a). Particles have been characterized with respect to DNA entrapment degree, swelling/deswelling behaviour, kinetics of DNA release, surface morphology, secondary structure and integrity of DNA in the particles (Figure 1b). Models for DNA release has been also described. These particles represent a conceptual step in the design and development of new nonviral vectors for the delivery of therapeutic DNA.

Fig. 1. Formation of DNA gel particles: a) CTAB-dsDNA particles and b) fluorescence micrograph of the lysozyme-dsDNA particles in presence of the fluorescence dye acridine orange.
INFLUENCE OF ELECTROSTATIC INTERACTION ON THE STRUCTURE OF PROTEIN GELS

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When proteins denature they often have a tendency to aggregate and if enough protein is present to gel. This process is widely utilized in food preparation where denaturation is generally induced by heating. A variety of gel structures is found in practice that ranges from fully transparent homogenous gels to highly opaque heterogeneous gels. The transparent gels consist of fine crosslinked strands of proteins, while the heterogeneous gels consist of aggregated micron size protein particles. The transition between the two types of gels appears to be induced by a reduction of the electrostatic repulsion either by reducing the charge density of the proteins by changing the pH or by screening the interaction by adding salt.

In order to understand the structural change it is necessary to study the systems over a broad range of length scales between about a nanometer to tens of microns. Here we will show how the gel structures can be characterized using a combination of scattering techniques and confocal scanning light microscopy (CSLM). We developed a method to quantitatively analysis of the CSLM images in terms of the pair correlation function, which could be directly compared with scattering results. We were able to track the changes of the amplitude and the correlation length of the concentration fluctuations with varying pH or ionic strength over many orders of magnitude.

Application of this methodology to the heat-induced gelation of the globular protein β-lactoglobulin showed that both the amplitude and the correlation length of concentration fluctuations increase dramatically over a narrow range of the pH or the ionic strength. The increase is caused by the reduction of the repulsion between the protein aggregates, which leads to increased concentration fluctuations and eventually to phase separation. The concentration fluctuations are frozen in by crosslinking of the aggregates. The structure of these gels is similar to that of binary solutions close to the critical point. Further weakening the interaction leads to the formation of dense protein domains that cluster and form a network. We believe that the dramatic change of protein gel structures induced by the appearance of critical fluctuations and micro phase separation is a general feature of many proteins.
PROTEİN-DİSPERSED NANOTUBES: pH EFFECT AND CONCENTRATION MEASUREMENT

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Dispersion and exfoliation of carbon nanotubes (CNT) by water soluble dispersants such as surfactant, polymer or protein, is a key step [1] towards the application of carbon nanotubes in composite materials [2], biochemical and biomedical applications. Upon dispersion, the solution phase separates into dispersed nanotubes in the supernatant and a precipitate phase including carbonaceous impurities but also nanotubes and dispersants. Yet, simple but accurate tools to measuring the concentrations of the constituents are not available. In most studies a comparison between concentrations of CNT suspensions is based on ocular observation or on UV-visible measurement of a featureless spectrum or at single wavelength. Such measurements are complex since both nanotube and most dispersants absorb along the whole UV-vis spectrum and an overlap of their signals occurs.

In this paper we employ chemometric techniques to evaluate the pH effect on the concentration of both dispersant (protein – bovine serum albumin, BSA) and single-wall nanotube (SWNT) from a full UV-visible spectrum of aqueous solutions.[3] We find strong correlation between the conformation of the protein and its dispersion efficiency.

References:
UPtake and release of positively charged peptides by poly(acrylic acid) microgels

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Lightly crosslinked polyelectrolyte gels can absorb oppositely charged substances to a large extent and release them upon swelling in response to external stimuli such as changes in pH or ionic strength. Therefore such systems have great potential as drug delivery vehicles, notably of peptide and protein drugs.

In this study, poly(acrylic acid) (pAA) gels (70-120 μm in diameter) was studied upon interaction with various homopolypeptides, such as polylysine (pLys), polyarginine (pArg) and polyhistidine (pHis). A number of antimicrobial peptide analogues were also included in the study. The deswelling/swelling behaviour of microgels upon peptide binding/release was investigated with micromanipulator-assisted light microscopy. Furthermore, the distribution of peptides in gels and in some aspects, the intraparticular peptide transport, was evaluated by confocal microscopy. The effects of peptide structure, size and charge density as well as of pH and salt concentration in the external solution were evaluated.

Peptide incorporation into oppositely charged gels was found to be influenced by the size of the interacting peptides [1,2] and to some extent also by the solution pH and salt concentration [1,2]. The peptide structure, not essentially related to the charge density, was shown to play a significant role and the deswelling response of pAA microgels upon interaction with peptides was in the order pLys > pArg > pHis, where pLys induced a larger and faster deswelling of microgel particles. Peptides rich in histidine could rapidly be released from the microgel network by a raise in pH, whereas some peptides rich in arginine and lysine were released after an increase in salt concentration.

References:
HYBRİD LİPİD/DNA SELF-ASSEMBLİES

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Non-covalent strategies are a powerful tool for the bottom-up preparation of functional nanomaterials. In this field surfactant self-assembly has a prominent role and presents a number of advantages over conventional covalent molecular architectures, such as the ease of preparation and the intrinsically stimuli-responsive character. These characteristics can be further integrated through clever design of amphiphilic building blocks with the incorporation of functional moieties [1].

Particularly relevant is the case where biological functions are combined with a lipophilic moiety. An important example is represented by nucleolipids, hybrid molecules composed of two chemical moieties, a lipid and mono or oligonucleotides. In these derivatives the nucleic bases provides an additional parameter to control spontaneous self-assembly, since specific interactions among the polar heads alter aggregation thresholds and modulate properties of the aggregates on the mesoscale [2,3].

Aim of this contribution is to present an overview of the structural properties of self-assemblies of phospholiponucleosides. Several examples, related to different interfacial curvatures, will be presented and in each case the effect of molecular recognition on structural parameters highlighted.

As a recent development, hybrid structures [4,5], formed by nucleolipid/nucleic acids, termed nucleolipoplexes, will be presented, and their structural properties as inferred from SANS combined with complementary techniques, discussed in terms of specific interactions.

References:
CONTROLLING AMYLOID BETA-PEPTIDES TOXICITY BY BIOCOMPATIBLE POLYMERS

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Mechanisms causing Alzheimer’s Disease (AD) are not yet established, although genetic and animal models have shown a causal role of Amyloid β-Peptide (Aβ) in AD. However, recent debate has focused on whether amyloid fibrils or soluble oligomers of Aβ are the main neurotoxic species contributing to neurodegeneration and dementia. One approach for preventing aggregation would be the conversion of the peptide conformation. Prior investigations indicate that polymeric nanoparticles offer strong advantages in modulating the secondary structure of the peptide [1,2]. These results have encouraged us to extend our work on polymeric nanostructures for conformational transformations contributing to the development of new therapies for these diseases.

Complexes of polyampholytes and dodecanoic or perfluorododecanoic acid were prepared [2] resulting in nanoparticles with hydrodynamic diameters ranging from 3 to 5 nm. The fluorinated nanoparticles induced α-helix rich structures in Aβ peptide, whereas their hydrogenated analogues were less efficient leading in most cases to aggregation or β-sheet formation, as determined by circular dichroism spectroscopy. The degree of fluorination, the hydrophilic balance and the charge density of the fluoropolymers, as well as the size of the nanoparticles in aqueous solution, are decisive for the interactions.

The impact of these structures on the Aβ-induced toxicity in cultured neurons was studied. We report that the fluorinated nanoparticles increased the Aβ-mediated MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazoliumbromide) reduction, which indicates a higher cell viability. The anti-apoptotic effect of the complexes was evaluated by determining the activation of caspase-3. This assay also confirms the decrease of Aβ-mediated cytotoxicity in the presence of fluorinated biocompatible complexes (Figure 1).

References:
INTERACTIONS OF NANOPARTICLES WITH CELLS: EXTREMELY RAPID KINETICS OF NANOPARTICLE UPTAKE BY LIVE CELLS, END POINTS AND MECHANISMS OF ENTRY.

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Interest is growing in the possibility of quantitative reproducible studies on the impact of nanomaterials on living matter. However, even for nanoparticle-cell interactions many issues are currently unresolved, with little understanding of relevant length and time scales for intracellular entry. Emphasis is placed on the role of physio-chemical control and in situ characterization of dispersions. A well-characterised system is studied with a range of techniques, including confocal microscopy, flow cytometry and live cell imaging to identify the interactions of model nanoparticles with different cell lines. Nanoparticle uptake kinetics are studied as a function of size, in the range 50-400 nm. Intracellular access of nanoparticles smaller than 70 nm was found to be remarkably rapid, saturating within a matter of minutes. Nanoparticle uptake is found to compete with equally rapid exocytosis. Live cell imaging reveals that significant numbers of nanoparticles reach sub-cellular organelles within tens of seconds, but when their source vanishes, many (but not all) are exocytosed. Competition and inhibition of particle uptake are also investigated, in order to shed light on the mechanisms involved. Broader implications of these observations are discussed.
A "FLUID CANTILEVER" TO DETECT AMPHIPHILIC BIOMOLECULES

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Label free techniques are now identified as relevant tools to detect any biological material which can not be grafted by a fluorescent tag. In this growing context, a new detection strategy is proposed here, based on the rheological resonance of a functionalized air/water interface to which biomolecules come to adsorb. The experimental technique addressed in this paper exploits the resonant behaviour of a capillary (quasi-standing) network made with harmonic waves promoted along a chemically-functionalised air-water interface. These cylindrical capillary waves are excited from an outer sharp wedge managed at the top of a vibrated glass cell (θ=5 cm) filled with water.

In this way, it is possible to set accurately the mean curvature of the excited meniscus, and consequently, to monitor the micrometric amplitude of the capillary meniscus waves. Unlike Faraday waves, such meniscus waves are harmonic and exhibit a linear behaviour even at frequencies where damped resonance is observed. These resonance frequencies are found to be mainly controlled by the dynamical surface tension and reveal to be quite sensitive to the biological content of the liquid surface. In particular, one finds that the radial wavenumber of one resonance mode is imposed by the cylindrical geometry, and hence, that it is possible to follow the time-dependent surface tension from transient shift of the resonance frequencies. To this purpose, a dispersion relation, valid for the linear regime, is jointly used with laser interferometry. This optical technique is specially developed in order to characterize the surface elevation at the centre of the cell, which allows us to follow in real time the resonance frequencies and therefore to follow the dynamical surface tension. The sensitivity of this resonant technique is found high enough to apply as an in situ alternative to the well-known Cantilever technique. To illustrate this, use is made of a air/water interface functionalized by cationic (DOGS) lipids whose hydrophilic termination is able to link with DNA strands (involvement of a spermine group). A dedicated data processing of the transient surface aging due to DNA capture is presented.

Finally, the measurement technique is found to discriminate between single- and double-stranded DNA, initially solubilised within the water subphase.
HYDROLYZABLE CATIONIC AMPHIPHILES IN VECTORS FOR GENE THERAPY

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In recent years there has been an increasing interest in gene therapy, i.e. various therapeutic methods applied to supplement a defective gene with a functional one, and this medical approach is currently investigated in numerous clinical trials. Successful gene therapy is a multi-step process that involves compaction of DNA into a form that can be delivered to a cell, transport over the cell membrane, release of the DNA inside the cell, and ultimately expression of the gene. To bring about these events, a carefully chosen carrier, or vector, is applied. Traditionally, gene therapy has been performed with viral vectors, but in recent years an increasing number of promising reports on using vectors based on cationic amphiphiles have been presented in the literature. Amphiphile-based vectors, as compared to viral ones, have the potential to carry a higher load of DNA and have a lower propensity to cause an immune response. However, the use of cationic amphiphiles for gene therapy is limited by the fact that many such compounds show a non-negligible toxicity.

Esters of the amino acid betaine and long-chain alcohols show a physicochemical behavior in aqueous solutions that is very similar to that of conventional cationic surfactants, but due to their structural resemblance of natural lipoaminoacids they can be expected to show a better biocompatibility. Characterization of complexes of DNA and surface active betaine esters, with respect to physicochemical behavior as well as biological activity, is ongoing. An overview of the results will be presented.
EFFECT OF CHIRALITY ON NANOASSEMBLIES

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Chirality plays a crucial role in molecular recognition, and especially in biological systems. Alkanoyl-L-(+)-Ascorbic acid esters act as radical scavengers like Vitamin C (Figure 1), and can be easily dispersed in hydrophobic or aqueous media. We synthesized single chain, double chain, and bolaform surfactants that bear one or two L-(+)-ascorbic acid residues as polar headgroups. Depending on their structure and temperature, these derivatives form different nanoassemblies in water. Single chain surfactants (L-ASCn) produce micellar solutions (for $n=8$, 10) or gels (for $n \geq 11$), and upon cooling form hydrated crystalline phases (coagels) [1]. The bolaamphiphile forms monodispersed nanotubes in aqueous dispersions [2], while the more hydrophobic double chain surfactant produces stable organogels [3]. These nanoassemblies have been carefully studied through different techniques [1-4].

Recently we explored the properties of single chain surfactants that carry a D-(-)-Isoascorbic acid moiety (Figure 2) as polar headgroup. Although the D-epimer has the same antioxidant power of L-Ascorbic acid, however its biological activity is reduced to 5%. The amphiphilic derivatives D-ASCn produce the same kinds of nanoaggregates in water, but present significantly different properties from the epimeric L-isomers. Interestingly, D-ASCn and L-ASCn produce eutectics in the pure and in the coagel state. Here we report a review of the previous investigations, and the results of a preliminary study on the aggregation of D-ASCn single chain surfactants in water, and of their mixtures with the L-ASCn epimers, through SAXS, XRD, DSC, SEM, and conductivity experiments.

References:
NATURE’S LUBRICANTS: FRICTION AND SURFACE FORCE PROPERTIES OF PROTEIN-BEARING SURFACES

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Certain natural protein-bearing surfaces, such as knee cartilage and tooth surfaces, demonstrate excellent lubrication and wear characteristics [1]. To deduce the origins of these favourable characteristics, and subsequently mimic or control them, an understanding of the molecular properties and solvent interactions that govern them is necessary.

This study focuses on biolubrication of oral surfaces, though the conclusions are applicable more generally. A Surface Force Balance (“SFB”) was used to study the load and friction properties of adsorbed human whole saliva and purified protein fractions relevant to oral lubrication, such as mucin and statherin. The SFB allows the measurement of absolute layer thickness and friction properties over a macroscopic contact area, and this study is the first to use it to investigate the behaviour of these proteins and whole saliva under shearing loads. In particular, to investigate the role of mucin in boundary oral lubrication, a heavily-glycosylated polyampholytic form of pig gastric mucin (MW 564 kDa), with a well-characterised molecular structure and high purity [2], was measured in the presence of added salt and no-added salt environments.

The results show that the human whole saliva and adsorbed proteins are capable of lubricating otherwise strongly adhering mica substrates. For contact pressures of up to 0.66 MPa that are relevant to tongue-palate/tooth interactions [3], low friction coefficients in the region of 0.04 were measured for mucin. However, at higher pressures more typical of tooth-tooth contact [4], the friction coefficient increases (attributed to bridging phenomena) which points to limitations of these kinds of adsorbed polyampholytes as boundary lubricants. A clear shift in mucin properties was also visible when salt was added, with the adsorbed molecules now lying flatter and less capable of efficient lubrication. These results will be examined in the context of those obtained for statherin and whole mouth saliva. The implication of the results on biolubrication processes within the oral cavity and in general, including the relevance to other highly glycosylated proteins such as lubricin, will be discussed.

References:
SUPRAMOLECULAR ASSEMBLIES FORMED BY AMPHIPHILIC PEPTIDES BOTH IN WATER AND IN OCTANOL

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Surfactant-like peptides – especially intrinsically amphipatic peptides – represent a new class of self-organizing surfactants, capable of forming a wide variety of supramolecular aggregates in water like micelles, vesicles, tubules, fibers [1-4]. They are of particular interest when studying selective ion separation using complex fluids: their molecular structure can be easily and finely tuned giving access to large libraries; they ensure ion recognition and transport in biological systems due to their complexant properties and their 3D-arrangement.

We aim at using such bio-inspired surfactants for studying selective ion separation in liquid-liquid extraction, both phases being complex fluids. We have designed a series of peptides with close molecular structures and which are soluble both in water and in organic solvents like octan-1-ol. We will present here first experiments showing that these compounds are surface-active in water and self-organize in colloidal suspensions both in aqueous and in organic solutions. Depending on their hydrophobicity they can even form strong organogels [5-6].

References:
TOWARDS THE SYNTHETIC LUNG SURFACTANT: INTERACTION OF DPPC WITH CATIONIC FLUOROCARBON HYDROCARBON SURFACTANT

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The prerequisite for functional lung breathing is a reduced surface tension at the end of the exhalation. This function is accomplished by the lung surfactant, which forms a thin film at the air/water interface at the inside of the alveoli [1]. Lung surfactant is a secreted product that consists of a complex mixture of approximately 90% lipid (mostly DPPC, Dipalmitoylphosphatidylcholine) and 10% protein by weight [1]. The isolated four lung specific proteins are called as SP-A, SP-D, SP-B and SP-C. DPPC is not able capture the interfacial behavior of natural mixture by itself. The hydrophobic proteins (SP-B and SP-C) in natural mixture helps to disrupt the phospholipids bilayers and aggregates, thereby facilitating the formation of the monolayer and resprreading of the collapsed phase, increasing the adsorption rate of DPPC to the interface and regulates the cyclic process to minimize the hysteresis. In literature, there are several studies in which two-component systems made of DPPC and hydrogenated or perfluoroalkylated fatty acids have been investigated [2,3]. Recently, hybrid surfactants having fluorocarbon chain in its structure are introduced but they have miscibility problem which is could be important to obtain adequate surface elasticity and viscosity. We synthesized a new fluorocarbon hydrocarbon hybrid cationic surfactant called as F8C18N \((\text{CH}_3(\text{CH}_2)_{17})^+\text{N}^+((\text{CH}_2\text{CH}_3)_{12}(\text{CH}_2)_{3}(\text{CF}_2)_{7}\text{CF}_3)\text{I}^-)\) which is planned to be use with DPPC to capture the behavior of natural lung surfactant. Langmuir isotherms of pure DPPC, F8C18N and mixture of DPPC + F8C18N (0-50 % weight) are obtained at 20 °C and 37 °C using water and saline solution (Tris buffer + 150 mM NaCl). Addition of F8C18N results in the increase at the area per molecule occupied at the interface where the liquid condense phase is seen. Moreover, liquid condense / liquid expand phase transition disappeared. This disappearance will be related with the increase at the elasticity of the interface which is one of the essential properties of a lung surfactant replacement. The elasticity measurements of DPPC+ F8C18N mixture show that addition of 30 % F8C18N gives rise to increase at the elasticity of the interface from 200 mN/m to 300 mN/m at surface pressure of 40 mN/m. The F8C18N is not able to increase the surface elasticity by itself. This indicates the miscibility and synergistic interaction of DPPC and F8C18N. The hybrid molecules presented in literature were not successful in forming ideal mixtures. The new hybrid molecule presented in this study is also successful in lowering hysteresis of the cyclic process. The surface elasticity and hysteresis are not evaluated simultaneously before to our knowledge.

References:
BLOCK COPOLYMER MICELLES WITH COMPLEXED METALLACARBORANES IN CORES

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Polyhedral metallacarboranes have been recently recognized as potent inhibitors of HIV protease. They are characterized by exceptional hydrophobicity, rigid geometry, partially delocalized negative charge, ion-pairing behavior and strong acidity of conjugated acids. Some time ago we reported a strong association tendency of metallacarboranes and their bioconjugates in aqueous solutions [1,2]. Quite recently we started to study interactions and formation of high molar mass complexes of metalocarboranes (mainly of COSAN – see Schematics I) with water-soluble polymers. In this presentation, we report on the formation of multimolecular micelles of polyoxyethylene-block-poly(methacrylic acid), PEO-PMA as a result of the formation of insoluble COSAN-PEO complex.

We studied the interaction of the negatively charged COSAN anion with PEO, PMA and PEO(30k)-PMA(30k). We found that it does not interact with PMA, but it forms a complex with PEO. This complex is fairly soluble in salt free solutions, but it precipitates in NaCl containing solutions (I = 0.03 – 0.1 mol/L). Mixing the aqueous COSAN (Na salt) and alkaline PEO-PMA solutions leads to the formation of fairly large, but reasonably monodisperse nanoparticles with complex COSAN-PEO cores (hydrodynamic radius, \( R_H \), measured by dynamic light scattering ca. \( 10^2 \) nm, see Fig. 1).

The above outlined behavior can be explained by the results of quantum mechanics calculations which predict that H atoms attached to B bear a non-negligible negative charge [3,4] and form dihydrogen bonds with positively charged hydrogen atoms (in OH, NH and O-CH₂). Experimental studies are in progress and new results will be reported at the ECIS conference.

References:
MONITORING THE POLYMER CONFORMATION IN AQUEOUS SOLUTION BY FLUORESCENCE RESONANCE ENERGY TRANSFER

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The fluorescence resonance energy transfer (FRET) is a technique commonly used to investigate organized media like micelles, liposomes, polymers, proteins, and mixtures thereof. FRET entails transmission of energy from an excited donor to a ground state acceptor located in close proximity (< 10 nm). The distance and orientation between the donor and acceptor governs the efficiency of the energy transfer. Naphthalene (Np) and pyrene (Py) are known to interact as energy donor (Np) and energy acceptor (Py) in a FRET process with a characteristic distance, $R_o$, of 2.9 nm. We used this technique to monitor the interactions appearing in aqueous solution between the chains of poly(acrylic acid) (PAA) separately labeled with pyrene (PAA-Py) and naphthalene (PAA-Np). When the distance between the chromophores was within the range of FRET, excitation at 290 nm resulted in emissions from both Np* ($\lambda_{em}$ 310 to 400 nm) and from Py* ($\lambda_{em}$ > 380nm) excited by energy transfer from Np*. Excitation at 346 nm resulted in only the emission from directly excited pyrene, with no contribution from naphthalene. Steady-state fluorescence spectra of solutions containing PAA-Py and PAA-Np were monitored as a function of pH. A decrease in the Np* emission by energy transfer to Py was observed as the polymer solution was brought from acidic to alkaline pH. Although the concentration of the polymers in solution was far below the overlapping value, the FRET augments with pH and proves the entanglement of chains from different macromolecules. Other aspects concerning this phenomenon and factors that affect it will be revealed during the presentation.
COMPETITIVE SOLUBILISATION OF MODEL LOW-MOLECULAR-WEIGHT ADDITIVES BY CATIONIC SURFACTANT MICELLES AT LOW ADDITIVE AND SURFACTANT CONCENTRATIONS STUDIED BY CALORIMETRY AND $^1$H NMR SPECTROSCOPY

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The dissolution of scarcely or moderately water-soluble substances into aqueous solution by the action of surfactant self-assemblies to an extent exceeding their normal solubility in water, commonly called micellar solubilisation, is a complex phenomenon. For a given surfactant type and concentration in aqueous solution, the depth of additive penetration into the surfactant aggregate and its effect on the micelle size/shape depend mainly on the hydrophobic-hydrophilic character of the solubilisate and its overall content in the system [1].

The intention of the present work was to study the competition between phenol and another low-molecular-weight additive moderately soluble in water (i.e., butan-1-ol, heptan-1-ol, or heptanoic acid) for heterogeneous solubilisation sites within cationic micelles formed by hexadecyltrimethylammonium bromide (HTAB) in aqueous solutions at low concentration, close to the CMC. To preclude any significant changes in the micelle shape/size, the additive content was kept much below its critical phase-separation concentration, thereby allowing each solubilisate to behave as a probe. Titration calorimetry and $^1$H NMR spectroscopy were the main experimental techniques used to shed light on interactions of various additives with micellar aggregates and among themselves [2,3]. Adaptation of the research methodology to the small concentrations employed was necessary, especially in the case of $^1$H NMR.

One important result of this study was to show the difference in the micellisation and solubilisation pathways between H$_2$O and D$_2$O used as solvents in various experiments. The precise solubilisation mechanism was dependent on the composition of the system studied and had a net competitive character. For various additive couples, the competition between two solubilisates was monitored in function of the overall phenol content.

References:
INVESTIGATION OF OIL SOLUBILISATION IN COPOLYMER MICELLES – DEPENDENCE ON THE INTERPLAY BETWEEN THE POLARITY OF THE OIL AND THE COPOLYMER ARCHITECTURE

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The solubilisation of oils of varying polarity in block copolymer micelles in aqueous solution has been studied for the case of triblock ethylene oxide / propylene oxide polymers (Pluronics, PEO-PPO-PEO), polyisobutylene-b-polymethacrylic acid (PIB-PMAA), and polybutadiene-b-polystyrene-b-polyethylene oxide (PB-PS-PEO). For that purpose aliphatic and aromatic oils, esters, and alcohols were employed.

For the case of the Pluronics pronounced effects on the critical micellisation temperature (cmt) are observed, where the state of aggregation was studied by means of fluorescence spectroscopy, dynamic light scattering, and differential scanning calorimetry (DSC). The shift of the cmt to lower temperatures is not only directly related to the amount of solubilised material but also strongly correlated with the type of oil, especially its polarity. Enthalpy and entropy of micellisation were calculated from the concentration dependence of the cmt and they correlate with the type of solubilisate employed. The process of micellisation becomes less endothermic by the presence of solubilisate and this effect is more pronounced for more polar solubilisates.

The detailed structure of the formed aggregates was determined by SANS measurements and a systematic correlation between the type of solubilised oil and the aggregate size and structure are drawn. Depending on the polarity of the solubilised oil the oils are located in various regions of the block copolymer micelles. This becomes particularly interesting for the case of the triblock terpolymer PB-PS-PEO. This polymer forms spherical micelles with two different regions in the hydrophobic core. Accordingly one has two different solubilization sites within the micellar core. Depending on the oil added it becomes either solubilised in the core centre or in the shell region. That affects the packing parameter and can lead to a solubilisate induced sphere-to-rod transition or simply to a swelling of the shell, depending on the solubilisation site. In general, it is observed that blockcopolymer micelles are much more selective with respect to their solubilization properties compared to conventional surfactants.
FROM MICELLES TO MICROEMULSIONS, GELS AND RESPONSIVE NANOMAGNETIC GELS: WHEN HARD AND SOFT MATTER MERGE TOGETHER

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Micelles and microemulsions are some of the most used systems in detergency and in several other applications. The first scientific paper on nanoparticles dates back to Faraday time. Micelles and nanoparticles share a common size domain but their conjugation in a composite system is practically unexplored, neglecting the use of complex fluid as nanoreactors for tailored production of nanoparticles. Gels are used in several applications but usually are not associated to microemulsions or nanoparticles. In this talk I will report some illustrative examples showing how complex responsive system with outperforming properties can be obtained by merging micelles, gels and nanoparticles and by tailoring the properties of the individual systems employed for the fabrication of the responsive systems. The examples refer to cleaning of precious artworks but can be easily adopted for more common applications.
UNDERSTANDING THE GROWTH MECHANISM OF WORM-LIKE MICELLES COMPOSED OF TRİ-BLOCK COPOLYMERS

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The tri-block copolymer P123 (EO₂₀PO₇₀EO₂₀) is used in the synthesis of nanostructured mesoporous silica materials, such as SBA-15 [1]. The synthesis of SBA-15 typically starts with the formation of spherical micelles, which, during silica hydrolysis and condensation, are converted into long cylindrical micelles. The micelles act as soft templates, resulting in silica with hexagonally ordered mesopores, after removing the micelles. It is highly probable that the kinetics of the sphere-to-rod transition versus the kinetics of silica hydrolysis and condensation determines the final properties of the inorganic materials. Previously, we have shown that P123 forms worm-like micelles in the presence of KCl and ethanol. Both additives are usually present in the synthesis mixture [2]. This new study examines the kinetics of the sphere-to-rod transition of the P123 micelles induced by the same additives. Dynamic light scattering (DLS) and cryogenic transmission electron microscopy (Cryo-EM) are the techniques used.

The growth process of the worm-like micelles has two distinct regions that can be described as nucleation and actual growth to equilibrium. The duration of the nucleation stage depends on the solvent quality. The actual growth takes place once there are a significant number of large enough micelles. The wormlike micelles have a smooth and irregular caterpillar-like structure consisting of fused, still spherical, species. Additionally, a single relaxation time was found for all growth curves, which decreases with increasing surfactant concentration. The growth curves collapse into a master curve, when shifted by the nucleation time, indicating that the actual growth process of the micelles in all samples occurs through the same mechanism. Based on the obtained results, we propose that the transition of the spherical micelles to long rods proceeds through random coagulation and fragmentation reactions involving micelles of different sizes [3].

References:
NANOEMULSION FORMATION BY A NEW, LOW-ENERGY METHOD

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Nano-emulsions [1,2] are characterized by a droplet size between 20 and 500 nm. They are not thermodynamically stable but they can possess long term kinetic stability if adequately prepared. Due to their small dimensions, nano-emulsion preparation requires a large energy input. Two different approaches can be used: low energy methods (as the phase inversion temperature method, PIT) or high energy methods (high-shear stirring). The latter have higher costs and usually generate unstable nano-emulsions, with larger size droplets and of wider size distribution. The former are potentially of lower cost, but general low energy procedures to make nano-emulsions do not presently exist, and often the nano-emulsions generated have limited stability.

In this paper we describe a new, simple low energy method which generates very stable nanoemulsions (both water-in-oil and oil-in-water systems) with a radius of about 20-40 nm. The preparation consists of two steps. In the first step a concentrated dispersion is prepared by mixing an equal quantity of water and oil and adding a mixture of surfactants (about half of water amount). Changing the surfactants ratio, (the HLB of the mixture) different kinds of concentrated dispersions (precursors) are obtained. In the second step the concentrated dispersion is diluted in what is the external phase of the finale nano-emulsion. That is, it is diluted with water to obtain an oil-in-water nano-emulsion, and with oil phase to obtain water-in-oil nano-emulsions. Key to generating the nano-emulsion is a change in the HLB of the surfactants mixture during the dilution. Choosing the right HLB precursor, and the right final HLB, very stable nano-emulsions (till one year), can be generated, characterized by small and monodisperse drop sizes. The method reported has been employed with different surfactants, oils and brine phases, opening a route to the preparation of nano-emulsions of interest in many applications, including several in the petroleum industry.

References:
DENSE OİL-WATER EMULSIONS – STRUCTURE AND DYNAMICS STUDIED BY LIGHT SCATTERING

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Dense Emulsions are widely used in many applications, but it is difficult to study their structure and dynamics by optical methods due to the high turbidity of such systems. Multiple scattering is strong and makes light scattering experiments difficult to perform and to analyze. We were able to study such dense emulsions by static light scattering using a special flat cell light scattering instrument [1,2]. This methodology could also be applied to other dense dispersions [3].

It is even more challenging to measure the dynamics via dynamic light scattering in such turbid systems [4]. For very high volume fractions a gelling may be observed and it has to be checked if a real glass transition (ergodic to non-ergodic transition) can be found for the formable oil-water emulsions [5]. For this purpose it was necessary to develop a new instrument combining the thin flat cell, 3D cross-correlation optics and the echo-technique in one system [6]. First results show only a slowing down of the dynamics but not a real non-ergodic system.

This finding is agreement with the results from shear-crystallization experiments. Oil-water emulsions do not crystallize spontaneously due to their polydispersity, however they do when sheared under controlled conditions. Once the shear is stopped the crystals start to melt. The melting kinetics depends on the volume fraction of the droplets [6].

References:
STABILITY OF CONCENTRATED MONODISPERSE EMULSIONS AND ITS RELATION TO THE INTERFACIAL RHEOLOGICAL PROPERTIES

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Despite the large amount of work devoted to the understanding of emulsion and foam stability, the prediction of emulsion and foam lifetime remains an unsolved problem. Understanding better the mechanisms of destabilisation is however mandatory for the improvement of the many technological processes involving emulsions and foams.

Emulsifiers are frequently surfactant molecules that adsorb spontaneously at the air or oil/water interface thereby reducing the interfacial tension. A monolayer is formed at the interface between coexisting phases. This monolayer can resist to deformations due to a finite elasticity but can also flow: it is viscoelastic in nature. Emulsion stability may vary considerably from one system to another, depending of the nature of the surfactants, the nature of both phases, and their volume ratio. We have used a variety of surfactants in our work: two non ionic surfactants (with ethylene oxide and glucose polar heads), four cationic surfactants (with the same polar head and different chain length) and 2 copolymers (PE/F127 and PE/F 68). The emulsions were made using alkanes of different chain length as oil phase.

We have studied the compression viscoelastic properties of surfactant monolayers by using the oscillating bubble/drop method in the frequency range 0.1-1 Hz and the propagation of capillary waves in the frequency range 100-1000 Hz (air/water interface). The shear viscoelastic properties were studied with a shear rheometer equipped with a bicone.

We have also studied monodisperse emulsions, prepared by application of a controlled shear, and measured the evolution of droplets diameter as a function of time (using laser granulometry). The evolution depends of the size of the drops, hence the necessity to work with monodisperse emulsions. We are preparing still more monodisperse emulsions (by a microfluidic technique) where we can visualise the different droplets. The time evolution is related to the different surface viscoelastic properties of the surfactant monolayers.
PICKERING EMULSIONS WITH BARE SILICA

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Stable o/w Pickering emulsions have been prepared with bare silica particles as stabilizer [1]. According to literature, the solid particles that stabilize Pickering emulsions are necessarily grafted (functionalized) with organic silanes in order to ensure the partial wetting conditions of the solid by both oil and water. Bare silica is thought too hydrophilic for being anchored at the interface; indeed emulsions prepared with most common oils and bare silica particles are not stable. We report that particles of bare silica (unfunctionalized) are efficient stabilizers for emulsions made with "polar oils", that is, organic liquids of low solubility in water but with moderately polar groups. Typical examples of such polar oils are diesters (diisopropyl adipate), small monoesters (ethyl acetate).

A close description of such emulsions is given, i.e. the typical droplet size, type and concentration of silica, assessment of the long term stability. The type of oils giving successful emulsions is precisely defined with the help of physico-chemical characterizations of their interaction with water and silica: partial wetting is shown by contact angle measurements, interfacial tension between oil and water is lower than 15 mN/m.

The role of silica at the oil water interface was assessed in comparative experiments where the silica content was varying both for o/w emulsions of polar oils stabilized with bare silica and of non polar oils stabilized with hydrophobic silica [2]. It is demonstrated that the droplet size is related to the silica/oil ratio, that adsorption of a dense layer of silica particles is an absolute requirement. Lastly, evidence of the presence of excess silica particles in the aqueous phase is given for high silica/oil ratios. Thus, analysis of the particle size distribution allows the detection of excess silica particle that are not anchored to the droplet surface above a threshold concentration of silica. The presence of such silica particles in water causes thickening of the emulsion. A detailed investigation of the rheological behavior is reported.

References:
CONFINEMENT OF DNA INTO WATER-IN-OIL MICROEMULSIONS

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Water-in-oil (WO) droplet microemulsions are thermodynamically stable suspensions of nanoscale water drops suspended in oil and stabilized by monolayer films of surfactant molecules. DNA can be readily dissolved into microemulsions stabilized by an anionic surfactant (AOT). We report a detailed study of the structural modifications of the microemulsion drops by varying the concentration and molecular weight of DNA and using various techniques such as quasielastic light scattering, small angle neutron scattering (SANS), electrical conductivity and surface tension. DNA is incorporated into large drops coexisting with small DNA-free drops, similar to those found in the DNA free microemulsion. The shape and the size of large drops depend on the amount of DNA dissolved in water, as well as on its molecular weight. This novel type of microemulsions could, beyond the potential of original shapes as templates for synthesis, be used to perform single-molecule DNA enzymatic reactions in small volumes of water around DNA chains.

Fig. 1. Probable picture of microemulsion containing DNA
TEMPERATURE DEPENDENCE OF THE DYNAMICS IN SUGAR SURFACTANT BASED BICONTINUOUS MICROEMULSIONS

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Neutron spinecho (NSE) spectroscopy and dynamic light scattering (DLS) are excellent tools to study dynamic processes like diffusive translational motions and undulations of the surfactant membrane in microemulsions \cite{ref1}. The low q-range observed by DLS allows to gather information about collective diffusional dynamics while NSE spectroscopy detects the bending undulations of the surfactant membrane on local length scales, much smaller than typical structural lengths in microemulsions. Up to now, all published NSE measurements devoted to the dynamics of bicontinuous microemulsions study the influence of the microemulsion composition or the addition of polymers enhancing the efficiency of surfactants \cite{ref2}.

In the present work a quaternary microemulsion system water / rapeseed methyl ester / sugar surfactant / pentanol is studied. Bicontinuous microemulsions based on these components are investigated in order to design environmentally compatible and low irritant decontamination media for the removal of toxic industrial compounds and chemical warfare agents. Compared to the CiEj surfactants an important feature of the behavior of such sugar surfactant based systems is the small influence of the temperature on the phase structure. The theoretical approach of Zilman and Granek \cite{ref3} allows the determination of the bending elasticity from the measured normalized intermediate scattering function $S(q,t)/S(q)$, which we measured at different temperatures. In the present contribution for the first time the ZG predictions with respect to the temperature dependence of the surfactant film dynamics are analyzed and discussed. For this purpose both scattering methods have to be used in combination.

References:
REVERSIBLE THERMAL GELATION IN CONCENTRATED STARS SOLUTIONS.

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The reversible gelation upon heating in the soft colloidal star polymers were reported few years ago for the first time. This system is driven by excluded volume interactions; however at higher concentrations arms begin to interpenetrate in order to reduce the osmotic pressure gradient. That leads to formation of clusters and to partial dynamic arrest of the swollen star [1,2].

We present here the reversible thermal vitrification studies of 1,4 polybutadiene star with arm functionality 122 and arm molecular weight 80k in intermediate quality solvent performed with Small Angle Neutron Scattering. To reveal the effect of jamming on the structure of single molecule both the form factor in the dilute solution and the form factor in the crowded solution above $c^*$, were systematically examined as a function of temperature. The star expands upon heating; thus the effective volume fraction increases which is a prerequisite for gelation. The temperature dependence of radius of gyration expansion is nearly linear up to gelation point where it starts to level off. The percolated state exhibits differences at high scattering vector lengths due to swelling of the peripheral blobs. As revealed by complementary structure factor measurements, it does not affect star-star distance, which implies that upon heating the overlap of the swollen stars arms is enhanced. That is accompanied by increase of the structure factor peak. Upon cooling the initial state is entirely recovered, however this process is very slow.

Finally the aging effect was examined at the gelation transition temperature. The form factor was found to be unaffected, unlike the structure factor, with the main peak growing and additional peaks forming. Structure factor peaks determined at and above transition temperature are larger than 2.8, the Hansen-Verlet criterion for freezing.

References:
Polymers with a reversibly associating end group at both ends (so-called telechelic polymers) can form physical gels which have a number of original features. First of all, the structures that these polymers form are of course not permanent, but transient, and their kinetics and appearance depend on physical parameters like concentration, temperature, etc. Hence, dilute micellar systems occur, as well as phase-separated and monophasic networks with gel-like properties. In this presentation we discuss the behaviour of two telechelic polymer systems: alkyl-endcapped polyethylene oxide (HE-PEO) and a 'de novo' biosynthesized protein (COLL-R-COLL) consisting of a random coil, water-soluble chain with two short collagen-like blocks at either end.

In concentrated HE-PEO solutions, the hydrophobic end groups assemble into small, micelle-like domains which can be seen as the node points of the network. When such a solution is slowly sheared, it behaves as a Maxwellian viscoelastic fluid with a relaxation time depending on the length of the hydrophobes; for C16, it is typically about ..., whereas for C18 it is ... At shear rates comparable to the (inverse) relaxation rate, the rate at which hydrophobes are extracted from the micellar domains increases, causing a rapid decrease in the relaxation time. As a result, the stress maintained by the system drops and starts to fluctuate erratically. In addition, velocity measurements show that the shear rate profile splits up into two (sometimes even three or more) bands. This is evidence that the network structure of the system is changing: the orientational distribution of intermicellar bridges probably becomes anisotropic, allowing for more bridges in the velocity than in the vorticity direction. A simple constitutive equation can be developed which captures the non-monotonic stress pattern.

When the interaction between the end blocks is increased, the relaxation time increases and the discontinuity in the shear rate profile can become very large, resembling a fracturing pattern. This happens for PEO with very hydrophobic blocks like fluorinated alkyls, but also for COLL-R-COLL. The end groups of this polymer form triple helices, which have relaxation times of the order ... at room temperature. As a result, the networks behave as gels that can break when sheared at the usual rates and to large deformations. In contrast, they creep very slowly when sheared gently, and they heal completely when left at rest after a breaking event.

Because each associated domain in this polymer consists of exactly three COLL strands, the network contains only two kinds of elements: nodes which are trifunctional, and dangling ends terminated by a loop. Assuming that the COLL strands associate reversibly, it is possible to evaluate the equilibrium distribution of loops and nodes, and to calculate both the concentration and the temperature dependence of the modulus. Very good agreement with rheological data is obtained.
THE BEHAVIOUR OF SURFACTANT GEL AND LAMELLAR LÍQUID CRYSTALS UNDER FLOW; CORRELATION OF NMR QUADRUPOLE SPLITTINGS WITH OPTICAL MÍCROSCOPY AND X-RAY DIFRACTION MEASUREMENTS DURING SHEAR TO GIVE DOMÁIN STRUCTURE

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Formulation is a key aspect to surfactant manufacture and the use of surfactants in formulated products is now commonplace. Most surfactants form liquid crystalline phases (mesophases) during processing and manufacture, and when mixed with water for use. This presentation concentrates on liquid crystals used in materials science, specifically detergents and personal care products, and the importance of linking surfactant chemical structure and flow properties. For this study a commercial non-ionic, lyotropic liquid crystalline material, C_{12-14}EO_3, has been selected. The self assembly of the surfactant in water leads to the formation of both the lamellar (L_α) and the gel (L_β) layer phases. The presence of a gel-lamellar coexisting region, where the two phases are intimately linked, has been observed. Further investigation revealed two gradual gel-lamellar phase transitions with surprisingly low energy changes. Subsequent studies within these regions revealed the gel phases formed were indeed bilayers with very distorted chains and so the complexity of the system continued.

Optical microscopy, rheology, X-ray diffraction, nuclear magnetic resonance (NMR) and rheo-NMR have all been used to study the highly non-uniform flow which occurs in the mesophase material. Together these techniques allow the characterisation of this irregular flow, relating the rheology with the microstructure of the surfactant. Significant morphology changes are observed during shear measurements in both the gel and lamellar phase.

The effect of shear on the lamellar phase has been studied in depth; at low shear rates there is parallel alignment of the lamellae to moving surfaces and at high shear rates the formation of liposomes. Initial studies (using an optical shear cell) observe that the flow is irregular, with slow moving “lumps” being separated by a small fraction of rapidly moving material where most of the shear occurs. Shear measurements within the intermediate two phase region have also been completed. A number of quite unexpected, novel, results were encountered, for example

- In the gel-lamellar coexistence region only a single NMR spectrum is observed, whilst separate X-ray diffraction patterns occur.
- Water ordering in the gel phase appears to be generally smaller than for the lamellar phase, unlike the accepted pattern of behaviour.
- Observations of varying alignment and orientation states indicate structural reordering although the origins are, as yet, unknown.

Additional studies were made in samples containing a small concentration of a cationic surfactant. This is expected to cause a large increase in the inter-layer repulsions and could also promote composition differences within the differently flowing regions. While the results are broadly similar to those of samples without added ionic surfactant some significant differences observed, including the rapid re-mixing of the CTAB. As this mixed surfactant system is similar to industrial formulations the results are appropriate for application to product processing.
STUCTURAL ORDERING AND PHASE TRANSITIONS IN THERMO RESPONSIVE CHARGED MICROGEL COLLOIDAL SUSPENSIONS

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Recently, thermo responsive microgel colloids of poly(N-isopropylacrylamide) (PNIPAM) have shown to be an excellent model to investigate phase transitions [1,2] in soft sphere colloids. However, if the polymer chains of the microgel carry ionic groups (such as acrylic acid, AAc), the later dissociates in aqueous medium leading to a charged microgels (PNIPAM-co-AAc). This charged microgel is sensitive to pH, temperature and ionic strength [3]. In the present article, we studied structural ordering and phase transitions in the above mentioned charged microgel suspensions with respect to volume fraction and temperature at different pH (both < and > pK\textsubscript{a} of AAc) using light scattering.

The structure factor of the liquid ordered suspension obtained from light scattering at high pH (> pK\textsubscript{a} of AAc) was analysed by hypernated chain model and a screened Coulomb potential. The obtained effective charge was found to be smaller than the charges obtained by titration by a factor of 10\textsuperscript{2}. This liquid like ordered suspension under complete deionization underwent a phase transitions to a crystalline order above a effective volume fraction, $\phi_{\text{eff}} = 0.012$ (see Fig. 1). The effect of pH and temperature (> pKa) were found to be independent of the average interparticle spacing (obtained from experiment).

But structural ordering of microgels below pKa showed the freezing transition to occur above $\phi_{\text{eff}} > 0.4$. The temperature effect showed the increase in the average interparticle spacing due to decrease of the hydrodynamic radius of the particle. However, at low pH ($\leq 3$), the liquid ordered suspension showed a fluid-solid coexistence at high temperature (above LCST of PNIPAM, 31°C) and the corresponding phase behavior in non-interacting suspension showed formation of homogeneous clusters at above LCST. We construct a phase diagram as a function of volume fraction and temperature below and above pKa and these results were compared with that of the phase diagram of the usual charged and hard sphere colloids. We understood this on the basis of a long-range coulombic forces dominating above pKa while a weak repulsive and a strong attractive force dominates below pK\textsubscript{a} at high temperature. We hope in single system, phase transitions can be studied by tuning the interaction potential over a wide range.

References:

Fig.1. Scattering Intensity verses scattering vector of microgel suspension in liquid ordered state (black curve) before deionization and in crystalline state (red curve) after deionization using ion-exchange resin. Inset figure is the picture of the microgel colloidal crystal showing irredescence to visible light. $\phi_{\text{eff}} = 0.02$. 

But structural ordering of microgels below pKa showed the freezing transition to occur above $\phi_{\text{eff}} > 0.4$. The temperature effect showed the increase in the average interparticle spacing due to decrease of the hydrodynamic radius of the particle. However, at low pH ($\leq 3$), the liquid ordered suspension showed a fluid-solid coexistence at high temperature (above LCST of PNIPAM, 31°C) and the corresponding phase behavior in non-interacting suspension showed formation of homogeneous clusters at above LCST. We construct a phase diagram as a function of volume fraction and temperature below and above pKa and these results were compared with that of the phase diagram of the usual charged and hard sphere colloids. We understood this on the basis of a long-range coulombic forces dominating above pKa while a weak repulsive and a strong attractive force dominates below pK\textsubscript{a} at high temperature. We hope in single system, phase transitions can be studied by tuning the interaction potential over a wide range.

References:
INVESTIGATING SOL-GEL KINETICS WITH X-RAY AND LIGHT SCATTERING EXPERIMENTS COMBINED WITH MICROFLUIDICS

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Kinetics and structural data acquisition during sol-gel synthesis, especially during the first steps (10 ms-1 s), is of considerable interest for industry, and may lead to a better understanding of nucleation and growth. To investigate sizes and structures from the atomic to the colloidal scale, classical tools are X-ray and light scattering. However, Small Angle X-ray Scattering (SAXS) or Dynamic Light Scattering (DLS) are difficult to perform using classical means for probing small time scales. Microfluidics may overcome such difficulties. Indeed, droplets playing the role of microreactors (10 nL to 1 µL), can be easily engineered in a microfluidic device at the intersection between two immiscible flows. Performing sol-gel synthesis inside these droplets flowing through channels (size 10-100 µm) enables not only, to follow the reaction kinetics on-line (thanks to the time-position equivalence), but also to access to short times (a few ms) after the mixing of reactants. These microdevices (lab-on-chip) are generally made of elastomers, silicon or glass, using lithography techniques inferred from microelectronics. As these materials are not compatible with X-ray beams (weak signal/noise ratio, X-ray induced damages), SAXS has not been developed in this field. For other reasons, DLS has neither been adapted to microfluidics for on-line measurements (i.e without stopping the flow). Indeed, when fluids flow in a microchannel, because of the dimensions involved and due to velocity gradients, the Brownian diffusion and the shear-induced characteristic times are comparable. Therefore, the time extracted from DLS in a microchannel cannot directly provide the size with the Stokes-Einstein relation.

In this work, we show how to combine SAXS and microfluidics and how to overcome the difficulties to perform on-line DLS in a chip. For SAXS, we have developed original millifluiddic devices in polyimide, suitable to intense X-ray beams and we validated them with experiments performed at the European Synchrotron Radiation Facility (ESRF). Quantitative and structural data about the objects (from 5 to 500 nm) in the droplets were collected a few ms after the mixing of the reactants. Concerning DLS, by setting the diffusive volume size, we measured colloidal sizes under flow in the chip, 100 ms also after the mixing of reactants.

References:
UNUSUAL TRANSPORT PATTERNS OF COLLOIDS IN MIXTURES OF LIQUID CRYSTALS AND ISOTROPIC SOLVENTS

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Liquid crystals doped with low molecular weight isotropic solvents are characterized by coexistence of isotropic and nematic domains within a substantial temperature interval. When the mixture is cooled continuously through this interval, this gives rise to redistribution of the isotropic component between the nematic and isotropic phases, leading to diffusive solvent flow and to local concentration gradients. Local changes in composition may cause significant variations in interfacial tension between isotropic and nematic domains.

Using colloids with different properties (PMMA, silica) as tracer particles in mixtures of 5CB with small amounts of octane or tetrachlorethylene as isotropic solvent, we video-microscopically followed up single particle trajectories as well as the evolution of nematic domain growth throughout the phase transition.

Distinct colloid motion patterns could be discerned. Attraction towards nematic droplets was present at earlier stages of phase transition. Later, attraction was increasingly accompanied by an outward component of motion. The resulting convection-like motion pattern gave rise to colloidal “rims” around nematic droplets at a distance of several µm from the interface. Both the attractive and convective motion patterns were eliminated by solvent pre-equilibration of the PMMA colloids and absent when silica colloids were used. Therefore, they could be ascribed to direct interaction with solvent concentration gradients. The convective component of colloid motion could be explained by Marangoni convection due to variations in interfacial tension.

Advection to hydrodynamic flow on much larger length scales was also observed, typically during coalescence of nematic domains. Surprisingly, however, often the characteristics of attraction and “convection” coexisted with large-scale flow even for longer periods of time.

We demonstrated that transport mechanisms acting on the scale of micrometers, such as phase transition-induced local concentration gradients, can govern colloid motion even in the presence of much larger-scale flow. This property of low interfacial tension systems could be employed to generate novel structured colloidal materials.
PROBING THE PHASE DIAGRAM OF A COLLOIDAL SUSPENSION UNDER HIGH PRESSURE BY NEUTRON AND LIGHT SCATTERING

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We have applied small angle neutron scattering (SANS), diffusive wave spectroscopy (DWS) and static and dynamic light scattering (SLS and DLS) to investigate the phase diagram of a sterically stabilized colloidal system consisting of silica particles on which octadecyl-chains are grafted dissolved in toluene. The system exhibits a phase separation at about -3°C at ambient pressure in a volume fraction range between $\phi=0.05$ and 0.17. We have determined by DLS the pressure dependence of the coexistence temperature and the spinodal to be $\frac{dP}{dT}=77$ bar/K. Since this is a rather large value, the system properties can be nicely examined by using pressure variations. The curiosity of this system is that it shows a gel-line intersecting the coexistence line around the critical point being at a volume fraction of about $\phi=0.16$. We have accessed the coexistence line by DLS under pressure for dilute solutions with volume fractions lower than the spinodal concentration and have determined the stability limits by kinetic SANS experiments performing a pressure jump into the metastable and unstable regimes. The gel line was measured by DWS under high pressure using the condition that the system became non-ergodic when crossing it and we determined the coexistence line at higher volume fractions from the DWS-limit of turbid samples.
CHROMONIC LIQUID CRYSTAL FORMATION
BY EDICOL SUNSET YELLOW

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Chromonic mesophases are a well-defined group of lyotropic liquid crystals with very different structures from conventional amphiphiles. While extensive research has been dedicated to the field of surfactant liquid crystals, the structural and aggregation studies of chromonics have only emerged as a topic of interest within the last few years. The main objective of this research is to explore the molecular structure within aggregates of the Edicol Sunset Yellow dye. Multiple techniques, such as Optical Microscopy, multi-nuclear NMR (\textsuperscript{1}H, \textsuperscript{2}H, \textsuperscript{13}C, \textsuperscript{23}Na) and X-ray diffraction have been used in order to examine the solution and liquid crystalline phases. We also wish to determine the tautomeric form present in both dilute and concentrated solutions. The recent report by P.J. Collings [1] assumed the predominance of the azo form. We have measured and analysed \textsuperscript{13}C NMR spectra showing that the compound exists predominantly in the hydrazone form. \textsuperscript{1}H NMR helped to study the state of aggregation of the dye in solution with respect to variable concentration. The decrease in the chemical shift of the protons was observed as a result of raising the concentration, indicating the extent to which aggregation occurred over the range of compositions and providing evidence of the involvement of the whole dye molecules into the stacks. Remarkably, from proton NMR of the mesophases it is possible to obtain molecular order parameters using direct proton dipolar splittings. Optical microscopy allowed us to identify the liquid crystalline phases and to construct the phase diagram. X-ray diffraction data proved packing of the molecules into single molecule columnar aggregates. An unusual feature of the X-ray diffraction pattern of the mesophases occurred in the form of diffuse off-axis reflections at ca. 6.8 Å. It is proposed that these arise from “head-to-tail” molecular packing within the stacks, a result also predicted by recent computer simulation studies [2].

References:
RHEOLOGY AND SHEAR-INDUCED CRYSTALLIZATION OF HARD SPHERE GLASSES

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Under oscillatory shear, hard sphere colloidal glasses are able to assemble into a random FCC crystal structure with the (111) plane parallel to the velocity-vorticity plane [1]. The rheological properties of these high volume fractions are studied with particular reference to the rheological response of the shear induced crystals. Using practically monodisperse particles, we prepare shear-induced crystals under oscillatory shear and examine their linear and non-linear mechanical response in comparison with their glassy counterparts at the same volume fraction. It is evident that shear-induced crystallization causes a significant drop in the elastic and viscous moduli due to structural rearrangements that ease flow. For the same reason the critical (peak of $G''$) and crossover (overlap of $G'$ and $G''$) strain, indicating the onset of yielding, are smaller in the crystal compared to the glass at the same volume fraction. When, however, the distance from the maximum packing in each state is taken into account the elastic modulus of the crystal is found to be larger than the glass at the same free volume suggesting a strengthened material due to long range order. Furthermore, the microscopic particle rearrangements during the shear induced crystallization are followed by the technique of Light scattering Echo.

References:
THE PHASE BEHAVIOUR AND KINETICS OF ATTRACTIVE ROD-LIKE VIRUSES UNDER SHEAR FLOW.

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The phase behaviour of rod dispersions in equilibrium is well known and understood. These systems are very sensitive to external field, for example shear flow or magnetic field. It is therefore interesting to investigate the phase behaviour of a dispersion of rods affected by a shear flow [1,2]. The influence of shear rate, rod concentration and rod-attraction on the phase separation kinetics was investigated by time resolved Small Angle Light Scattering. From these experiments the non-equilibrium phase diagram for the isotropic to nematic transition as a function of shear rate and rod concentration has been determined. Both the *binodal*, which gives the shear rate and concentration where the dispersions become meta-stable, and the *spinodal*, which gives the shear rate and concentration where the dispersions become unstable, have been experimentally determined. We will show that the phase diagrams for all attraction investigated can be collapsed on a single master curve with a simple scaling. We gain further microscopic understanding of this phase behaviour by comparing the experiment with Multi-particle Collision Dynamic simulations (MCD).

**References:**

SPECÎFIC İON EFFECTS İN COLLOİDAL SYSTEMS – PRESENT STATE OF ART

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In the last years a Renaissance of Hofmeister effects has been observed. Significant progress in the description of specific ion effects leads to a new understanding of numerous phenomena in biology, chemistry, physics, and in particular in colloidal chemistry. Today, we are able to predict the consequence of ion exchange in complex systems nearly in a quantitative way.

The present contribution tries to resume the most recent achievements in this field and their consequences for colloidal and interfacial phenomena.

I will focus on the following points:

a) It is possible to establish a Hofmeister-like series of surfactant headgroups [1]. Together with Collins’ recent concept of “matching water affinities” [2] and the classical series of ions it is then possible to predict the interaction of headgroups with ions.

b) Examples of such predictions will be given for micellar systems, vesicles and liquid crystals in contact with different ions.

c) Potentials of mean force and distance dependent dielectric functions coming from MD simulations can advantageously be incorporated into the Poisson-Boltzmann equation to predict specific ion adsorption on surfaces of lipids and on electrodes. The fundamentals of this approach and experimental verifications will be given.

For a general survey of ion effects, see Ref. [5]. Selected examples of our further activities in this field, in collaboration with groups we are acquainted with are given in Ref. [6-11].

References:
SURFACE FORCES AND FRICTION PROPERTIES OF ADSORBED BOTTLE-BRUSH POLYELECTROLYTE LAYERS

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Water-soluble uncharged polymers and polyelectrolytes are of immense technological importance, both for rheology control and for modification of surface properties. The latter application includes such vastly different areas as control of colloidal stability, non-specific protein adsorption, cleaning applications and lubrication. In this presentation we will focus on interfacial properties of a class of water-soluble polyelectrolytes, bottle-brush polyelectrolytes, where side-chains are grafted along a polymer backbone. The presentation will be focused on a particular series of bottle-brush polyelectrolytes, denoted PEO₄₅MEMA:METAC-X, where the uncharged segments (PEO₄₅MEMA) contain a 45 unit long poly(ethylene oxide) side-chain and the METAC units contain a permanent positive charge. The value of “X” denotes the mol percentage of charged segments in the polymer architecture, and in the investigated polymer series this quantity has taken the values 0, 2, 10, 25, 50, 75, 90 and 100. Thus, the research spans the realm from an uncharged bottle-brush polymer, via charged bottle-brush polyelectrolytes, to a highly charged linear polyelectrolyte. We will demonstrate how the graft density and charge density of such polymers affect adsorption, surface forces and lubrication. It will be shown that the adsorption of this class of polymer onto negatively charged silica surfaces is due to a subtle balance of forces, including interactions between silica and ethylene oxide chains as well as electrostatic effects. On mica, on the other hand, only electrostatic forces drive the adsorption. Measurements of surfaces forces will be used to demonstrate the most suitable polyelectrolyte architecture for achieving good steric stabilization. It will also be shown that very favourable lubrication properties can be achieved for a large range of PEO₄₅MEMA:METAC-X compositions, and that the formation of an ideal brush layer is not a prerequisite for achieving low friction. The results will be discussed in relation to the energy dissipative mechanisms that control the friction properties.

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Fig. 1. The effective coefficient of friction as a function of polymer composition, measured using AFM with a flat mica surface and a silica colloidal probe. Langmuir 24, 3336, 2008
SURFACE TENSION OF ROOM TEMPERATURE IONIC LIQUIDS

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Organic salts with low melting points (below about 100 °C) are commonly termed ionic liquids (IL). These liquids have unique physico-chemical characteristics: no significant vapour pressure, low flammability, good thermal stability and wide useable temperature range. There is a large (and rapidly growing interest) in their use as “green” solvents in organic synthesis, catalysis, extraction, etc. Ionic liquids are highly concentrated electrolytes and have potentially important electrochemical applications (e.g. batteries and fuel cells).

In this study we have looked at the interfacial properties of several imidazolium- and pyrrolidinium-based ionic liquids. The surface tension at room temperature was measured with the pendant drop and Wilhelmy plate techniques. The interfacial tension of ILs against a series of alkanes was determined by the pendant drop method. The contact angles on smooth Teflon surfaces were measured with the sessile drop method. Commercial grade ionic liquids (Merck) were used without further purification and some of these contained significant amounts of impurities (mainly halides and water). Nevertheless the results were reproducible and amenable to a simple physical interpretation.

The surface tension of all ILs studied strongly correlates with their molecular volume. The dependence is adequately described by the scaled particle theory. The interfacial tension measurements against non-polar liquids allow the splitting of the surface tension into an apolar (Lifshitz–van der Waals, LW) component and an acid-base (AB) component. The Hamaker constants estimated from the LW components are in good correlation with the values calculated through the Tabor-Winterton approximation. The interpretation of contact angles measured on smooth surfaces further confirms these findings.
THE INFLUENCE OF SOLVOPHOBICITY AND BULK NANOSTRUCTURE ON SOLVATION LAYERS OF ROOM TEMPERATURE IONIC LIQUIDS CONFINED BETWEEN SURFACES.

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In a previous article we presented solvation force profiles for three room-temperature ionic liquids (ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and 1-ethyl-3-methylimidazolium acetate (C\textsubscript{2}mimAc)) confined between Si\textsubscript{3}N\textsubscript{4} tips and mica, silica and graphite measured using an atomic force microscope.\textsuperscript{[1]} The measurements revealed oscillatory behaviour in all cases, with the size of the oscillations corresponding to the physical dimension of the ion pair. The surface charge and roughness, and the orientation of cations at the interface were thought to be the critical determinants of solvation layer formation in ILs, but recent small angle neutron scattering experiments with selective deuteration have conclusively show that PAN and EAN possess nanoscale heterogeneity in bulk solution.\textsuperscript{[2]} This suggests that the surface acts to align the inherent solution morphology, rather than simply inducing structure, which allows the detection of many solvation layers by AFM. In this presentation we will examine these issues as well as present new data obtained using formate based protic ILs. This new data shows that incorporation of an alcohol moiety into the alkyl group of the cation disrupts solvophobic interactions and leads to a reduction in the number of detectable solvation layers.

References:
INTERFACIAL TENSION STUDIES OF CTAB AT TOLUENE-AQUEOUS INTERFACE IN THE PRESENCE OF BROMIDE IONS

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Tetraalkylammonium salts are major components of anion-selective membranes of Ion Selective Electrodes (ISE). The analytical signal of ISEs is generated through the charge separation at the interface between the ion selective membrane and the test solution. A typical anion-selective membrane is made of plasticized poly(vinyl chloride) and contains a long-chain tetraalkylammonium salt, e.g. tetraddecylammonium bromide. ISEs with such membranes display a selectivity pattern consistent with the Hofmeister series (so-called Hofmeister-selectivity pattern). However, the exact mechanism of ion partitioning and charge separation across the interface is not yet well understood [1]. Due to a significant surface activity of tetraalkylammonium salts used in ISEs, the interfacial mechanism seems to be a highly probable way to explain the response of ISE.

In this contribution we aim to present the interfacial tension studies of cetyltrimethylammonium bromide (CTAB) in the presence of common counterion electrolyte (NaBr) at toluene-aqueous interface. The latter constitutes a crude model of the polymeric membrane-analyte interface in real ISEs. The results will be interpreted using an ionic surfactant adsorption model applied previously to the air-aqueous interface by Warszynski et al. [2] The model takes into account co-adsorption of counterions in the Stern layer, thus, allows for the description of anion specific effects for adsorption of cationic surface active species. It also enables calculation of the electrical double layer potentials from the interfacial tension data. These results can be further compared to the potential difference generated across the polymeric membranes of real ISEs in the presence of CTAB and NaBr.

References:
THE SURFACE COVERAGE OF GEMINI SURFACTANTS: HOW ARE THEY BEST DETERMINED?

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The limiting surface coverage of gemini surfactants is an important parameter for understanding how these interesting surfactants pack at an interface. The standard method for determining surface coverage at the air/water interface is to use surface tension measurements and the Gibbs equation. There has been considerable confusion as to what is the correct prefactor to use in the Gibbs equation for any given gemini and ion association and/or premicellar aggregation have been suggested as factors that may be affecting the prefactor. In principle, measurements of solution properties such as conductivity can give information about the state of the geminis in solution but they are not sufficiently sensitive to be used quantitatively. The result is that the limiting packing of geminis remains uncertain.

Neutron reflectometry measures the surface excess directly without any assumptions. Values already published for a series of cationic geminis with varying spacer length show marked discrepancies from the surface tension values. We have now extended those measurements to solid/liquid interfaces and to a wider range of geminis, including geminis of different side chain length, ones containing fluorinated fragments, and geminis containing different counterions. The neutron results form a very consistent set of data but they indicate that considerable problems remain with the surface tension method, problems that cannot easily be resolved by supplementary conductivity measurements.
INTERACTIONS BETWEEN GEMINI SURfactants AND OPOsITELY CHARGED POLYELECTROlyTES AT THE AIR/WATER INTERFACE: A NEUTRON REFLECTIOn STUDY

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The interactions between a number of oppositely charged polyelectrolyte/surfactant mixtures at the air/water interface have been studied using neutron reflectometry. These strongly interacting systems adsorb as complexes, with layer thicknesses and amounts of surface surfactant corresponding to those of an approximate surfactant monolayer over surfactant concentrations ranging from above the cmc down to 1/1000 of the cmc [1]. Additionally, for some mixtures, adsorbed layers with an overall thickness of around 60 Å and surface excesses corresponding to 2 – 3 times that of a surfactant monolayer are seen, at high surfactant concentrations. These thick composite layers consist of an upper surfactant monomer-polymer complex with a further loosely structured surfactant bilayer adsorbed underneath. This type of surface complex is seen for mixtures containing the single-chained cationic surfactant dodecyl trimethylammonium bromide (C12TAB) with various anionic polyelectrolytes including poly(acrylic acid) (PAA), sodium poly(styrene sulphonate) (PSS) and DNA, all of which show very similar behaviour [2-4]. However, in the presence of the di-chained cationic Gemini surfactant 1,2-bis(dodecyldimethylammonio)hexane dibromide, DNA and PSS display very different adsorption behaviours [5]. The DNA/gemini mixtures show adsorption behaviour very similar to that of the DNA/C12TAB mixtures, with enhanced surfactant adsorption at low concentrations and multilayers at higher concentrations. However, the PSS/gemini mixtures adsorb much less strongly and the amount of Gemini at the surface is reduced relative to that in the absence of PSS. These differences in adsorption behaviour are attributed to differences in the molecular structure and flexibility of the two polyanions. PSS is relatively hydrophobic and flexible enough to form bulk phase polymer-micelle complexes with the Gemini surfactant at low surfactant concentrations, whereas adsorption of surface complexes is much less favourable, since the di-cations on the Gemini would require adjacent bulky pendant charges on the PSS to be oriented towards the surface. Thus, the surfactant is actually removed from the surface. In contrast with PSS, DNA has a far more rigid structure and the charges on the backbone are at fixed intervals; factors which make the formation of surface DNA-monomer complexes much more favourable than bulk phase DNA-micelle complexes.

References:
SURFACTANTS AT SUPERHYDROPHOBIC SURFACES 
IN AIR/WATER AND OIL/WATER SYSTEMS

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The adsorption properties of amphiphiles on water repellent solid surfaces, especially in 
conditions of extreme hydrophobicity, have recently attracted great interest both from 
fundamental and applied points of view.

The nature of the amphiphilic molecules and the solid substrate topography have been 
found to play important roles in influencing the surface properties. Superhydrophobic surfaces 
(water-contact angle greater than 150°), due to the small contact area shown when in contact 
with water, strongly reduce interactions with aqueous environment inhibiting adhesion 
phenomena and enhancing liquid drainage.

In this work superhydrophobic surfaces have been under investigation to study the effect 
of single surfactant solutions and mixtures on the wetting of these surfaces in air-water and oil-
water systems.

The behaviour in liquid-liquid environment has been studied as well opening the 
investigation to the role played by the partition coefficient and then by the solubility of the 
surfactants in the oil phase.

By acting on the surfactant type and concentration, the spreading of a drop on a solid 
surface featuring a specific hydrophobic property can be controlled confining the volume by 
modification of physico-chemical parameters.

References:
angle, Wettability and Adhesion 2008 Ed.K.Mittal-Brill VSP (The Netherlands) in press.
EFFECT OF HEAD GROUPS IN PHOSPHOLIPIDS ON MISCIBILITY WITH PARTIALLY FLUORINATED AMPHIPHILES AT THE AIR-WATER INTERFACE

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The miscibility of binary mixtures of fluorinated amphiphiles and phospholipids has been systematically investigated within the monolayer state [1–7]. In the previous studies, it has been reported that the partially fluorinated monolayer of (Perfluorooctylundecyl)-dimorpholinophosphate (F8H11DMP) is miscible with dipalmitoylphosphatidylcholine (DPPC) [2,3]. It is generally accepted that fluorocarbon chains and hydrocarbon ones are immiscible each other in the bulk. This is because of the entirely different field between air and liquid phases for hydrophobic chains. In the present study, effects of the head groups in phospholipids on the miscibility with F8H11DMP were examined in the monolayer state. The phospholipids used here were dipalmitoylphosphatidylethanolamine (DPPE), dipalmitoylphosphatidyl-N-methylethanolamine (DPPE-Me), and dipalmitoylphosphatidyl-N, N-dimethylethanolamine (DPPE-2Me). The binary Langmuir monolayers of DPPE/ and DPPE-Me/, and DPPE-2Me/F8H11DMP were investigated by surface pressure (\(\pi\) – area (A)), surface potential (\(\Delta V\) – A, surface dipole moment (\(\mu_\perp\)) –A isotherms, Brewster angle microscopy (BAM), and fluorescence microscopy (FM) to understand the effect of the head group. Monolayers were spread on 0.15M NaCl at 298.2 K. Furthermore, two-dimensional phase diagram was constructed by the collapse pressures against the mole fractions (\(X_{F8H11DMP}\)). The BAM and FM micrographs were also measured to support their miscibility.

References:
DYNAMIC FORCES AND HYDRODYNAMIC BOUNDARY CONDITIONS IN BUBBLE-SURFACE INTERACTIONS

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Dynamic forces between a bubble (~50 µm radius) [1] as it is driven at speeds up to 30 µm/s towards or separated from a smooth mica plate using an Atomic Force Microscope in 1 mM NaNO₃ and in the presence of added surfactants revealed different types of hydrodynamic boundary conditions at the air/water interface. In the presence of surfactants above the critical micelle concentration, the dynamic forces at all speeds and at film thickness in the nanometer scale can be accounted for by a combination of electrical double layer colloidal forces between the bubble and the mica, deformations of the bubble according to the Young-Laplace equation and hydrodynamic interactions as described by the Reynolds lubrication theory with no-slip boundary conditions [2] at the solid/water and air/water interfaces. This observation is similar to previous dynamic force studies oil drop-particle [3] and drop-drop [4,5] systems. However, in electrolyte (no surfactants), a new boundary condition at the air/water interface that involves the transport of trace surface impurities is required to account for variations of dynamic forces observed at different speeds and provide a direct connection between dynamics force measurements and surface transport effects at the air/water interface [6].

References:
DIRECT MEASUREMENT OF BUBBLE-PARTICLE INTERACTIONS
BY AFM – EFFECT OF SURFACE CHARGE

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Interaction forces between solid particles and air bubbles are of significant importance both for academic studies and practical application. For example in the flotation process one of the elementary stages is a formation of an aggregate between the particle and an air bubble. This aggregate formation is governed by hydrodynamic, capillary and surface forces. In our studies we have been mainly focused on the surface forces. A colloid probe AFM technique has been used to measure the interaction forces between an air bubble and a spherical, smooth hydrophilic particle. The forces of interactions between the air bubble and the particle have been studied as a function of simple (1:1) electrolyte concentration and also pH of the solution in order to determine the electrostatic component of the force. Furthermore, any change in pH of the solution influences the surface charge. Therefore, depending whether or not the solution pH was above or below the point of zero charge of the solid particle, and noting that bubbles bear a negative charge from very low pH values, the interaction between the same and oppositely charged surfaces could be investigated. In the case where the bubble and particle bear the same charge, rupture of the wetting film and the attachment of the particle to the air bubble did not take place and the electrostatic repulsive force depended strongly on electrolyte concentration. For oppositely charged bodies the wetting film ruptured forming a stable thin α-film and weak adhesion between the particle and an air bubble was observed (which corresponded to contactless flotation) [1].

References
DEGREE OF ENERGY TRANSFER DURING THE BUBBLE BOUNCING FROM WATER/GAS AND WATER/SOLID INTERFACES

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Prior to formation of a foam /or a bubble-grain aggregate the rising bubble needs to collide with liquid/gas or liquid/solid interface. Time-scale of the foam and wetting film formation and rupture depends on the kinetic energy of the rising bubble because of the colliding bubble bouncing, which prolongs the film syneresis and time of rupture. The bubble bouncing is a consequence of two simultaneous processes: (i) syneresis of the liquid film till its critical thickness of rupture, and (ii) exchange of the bubble kinetic energy into surface energy of the system related to shape deformation of the interacting objects. If the energy exchange is quicker than the film thinning then the bubble bounces from the interface.

The degree of the bubble kinetic energy transfer into surface energy during the bubble collisions with water/air interface and with hydrophilic and hydrophobic solid surfaces was studied, as well as the influence of the bubble kinetic energy (impact velocity) on properties of the thin liquid layers formed. The bubble impact velocity was tuned by either variation of the interface position in respect to the point of the bubble detachment or by applying the bubbles of different sizes. It was found that in the case of the collision with water/air interface (water surface) the degree of the bubble kinetic energy transfer into surface energy of the bubble shape deformation was only 20%, because major part of the energy was consumed by the water surface deformation. In the case of water/solid interface the loss of the kinetic energy during collision was significantly smaller. For hydrophilic solid surface (mica) the degree of the energy transfer was 90%, i.e. the collision was nearly elastic. However, in the case of hydrophobic solid surface (Teflon) the degree of the energy transfer was below 80%. This lower degree of the energy transfer during collisions with hydrophobic solid surface was attributed to the air presence on the surface. It was also found that the kinetic energy (impact velocity) had a profound influence on the time of the bubble rupture at water/air interface and the wetting film rupture at hydrophobic solid surface. The time of bubble rupture was increasing with the bubble kinetic energy and could vary by an order of magnitude, depending on the impact velocity.
DYNAMIC FILM DEFORMATION AND DRAINAGE BETWEEN DROPS

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The interactions between deformable droplets under driven conditions have been modelled by Carnie et al. [1] for both attractive and repulsive double-layer forces, including the use of asymptotic expansions to derive a boundary condition that takes into account the constant volume of the drops. The model has been successful when compared to experiments performed using the Surface Force Apparatus [2,3] and the Atomic Force Microscope [4].

The goal of this work is to understand the mechanisms of film drainage and coalescence between two droplets, as in Klaseboer et al. [5]. Using laser interferometry (Fig.1), the evolution of the film profiles of the interacting drops can be experimentally measured and compared to theory (see figures). Real experimental data of film heights suggests that the use of a complete theoretical model with dimple and rim formation must be used. Simplified theories, (Reynolds flat film) will yield incorrect results. The theory also explains recent experiments [6], where coalescence (and thus film drainage) is enhanced when the drops are being retracted from each other (the arrow in Fig.2).

Fig. 1 Film thickness fringes during drainage.                     Fig. 2 Film height at center (h0) and rim (hrim).

References:
STRUCTURAL AND ELECTRONIC PROPERTIES OF BIOLOGICAL MOLECULES BOUND ON ISOLATED NANOPARTICLES

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Surface modifications of nanoparticles (NP) with biomolecules, such as amino acids, permit new applications for sensors and diagnostics in life science. Therefore, it is important to understand in detail the interactions between nanoparticles and ligands. NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy is a suitable method for investigations of the local electronic structure of organic molecules and NP. However, the use of synchrotron radiation in such experiments leads often to significant radiation damage [1]. Key to the present research is to study the nanoscopic targets in a free NP beam [2]. This avoids any contact to a substrate as well as radiation damage. Biomolecule functionalized gold and silica NP are chemically prepared and dispersed in liquid media. For a comparison, pure NP consisting of small biomolecules such as amino acids, lipoic acid, and dihydrolipoic acid are directly prepared from dissolved species. The solutions or dispersions are sprayed into the gas phase and subsequently, the solvent is evaporated. The NP beam is aerodynamically focused in the size regime $r > 20 \text{ nm}$ in the interaction region with monochromatic synchrotron radiation [2]. Total electron yields are measured near inner-shell absorption edges. In all cases no radiation damage was observed, even when long integration times are needed. Especially, the present results indicate that the high sensitivity of the experimental approach permits studies on sub-monolayer species bound to free nanoparticles: Significant spectral shifts are observed indicating the occurrence of changes in electronic structure between the free and NP-bound biomolecules. Moreover, we observed that the NEXAFS spectra of monovalent surface-bound model thiols and bivalent thiol-bound biomolecules, such as dihydrolipoic acid, are significantly different. These changes in the electronic structure are discussed in detail and compared to results from model calculations.

References:


MODIFICATION OF NANOSILICA BY GRAFTING ONTO AND GRAFTING FROM BIOCOMPATIBLE AND BIODEGRADABLE MACROMOLECULES

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There is a great interest in developing methods suitable for manufacturing objects with surface properties adaptable to environment (e.g. exposing hydrophilic or hydrophobic surface elements to hydrophilic or hydrophobic exterior). Such properties are often desirable in case of materials for medical applications. Modification of solid supports is usually carried on either by grafting polymer chains onto or from surfaces of solid substrates (examples are described in Refs. [1,2]. In this presentation we report on modification of silica and glass (nanosilica and model glass plates) in a way allowing changes of their interfacial hydrophilic/hydrophobic properties in contact with hydrophilic or hydrophobic liquids. Modification of silica and of glass plates was did consist of grafting 3-glycidoxypropyl trimethoxysilane (GPS) onto silica (reaction with hydroxyl groups on silica surface). In this way epoxide groups were introduced. The next step included grafting of biocompatible polymers. Living poly(ethylene oxide) was grafted onto silica in reaction with epoxide groups. Active centers created in this way initiated polymerization of lactide. In result hydrophilic poly(ethylene oxide) and hydrophobic poly(L-lactide) chains were tethered to the surface. Depending on hydrophilicity of the liquid being in contact with modified silica the hydrophilic or hydrophobic chains were in expanded conformation. The resulting materials were characterized by photoelectron spectroscopy, wetting angle measurements and (in case of nanosilica) by $^{13}$C CP MAS NMR.

References:
MONOLAYERS OF LATEX PARTICLES: STRUCTURE, DYNAMICS AND THEIR USE AS PROBES FOR POLYMER MONOLAYER MICRORHEOLOGY

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Micro- and nanoparticles have attracted much interest as possible substitutes of surfactants and polymers as emulsion and foam stabilizers in food science, cosmetics, and pharmaceuticals [1]. Also they are increasingly used as building blocks of functional materials and for controlled drug delivery. In most of the cases the systems of interest are multiphase, and subject to strong mechanical perturbations (flow, stirring, etc.). Also, quite frequently the particles are trapped at the interface of those multiphase systems, with a trapping energy that may easily be thousands of times the thermal energy. The structure and rheology of the interfacial layers of these systems has been found to have a strong influence in the macroscopic behaviour (structure and rheology) of emulsions and foams. In the present work we have studied the structure of latex particles at the water/oil interface using videomicroscopy. Latex particles of diameters ranging from 1 to 5 µm have been used. The density of the monolayers has been modified from the dilute (gas-like) to the concentrated (solid-like) state, as shown in Fig. 1.

![Fig. 1. Top: Video images of structure of latex particles of 1 µm of diameter for three different states: left, gas-like; centre, fluid-like; right, solid-like. Bottom: The radial distribution function for the three states calculated directly from the video-images.](image)

From \( g(r) \) the attractive part of the interaction potential has been found to vary as \( V(r) \sim r^{-3} \), in agreement with some of the recent theoretical models [2]. Videomicroscopy has also been used to follow the Brownian trajectories of the particles at the interface [3]. From the trajectories it is possible to calculate the diffusion coefficient, and using the appropriate hydrodynamic theories one may calculate the interfacial shear viscosity, \( \eta_s \) [4]. One of the advantages of the particle-tracking technique is that it is possible to use micro-particles as probes for measuring the \( \eta_s \) of polymer monolayers. The values of \( \eta_s \) as a function of temperature has allowed us to point out the existence of a glass-transition in a quasi-two dimensional system: a Langmuir polymer monolayer. The value of \( T_g \) is much lower than that of the corresponding bulk system.

References:
DIRECTING SELF-ASSEMBLY OF NANOPARTICLES AT THE WATER-OIL INTERFACE

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The past decades have witnessed the tremendous progress in tailoring various materials into nanoscale objects with defined size, shape, and surface chemistry. Self-assembly of nanoscale objects allows not only utilization of their intrinsic size-dependent physicochemical properties but also generation of novel collective properties arising from the inter-particle interaction. The present talk will highlight the recent achievement on using water/oil interfaces as platform to direct self-assembly of nanoparticles.

By coating with ligands bearing appropriately hydrophobic termini such as ester group, nanoparticles can be imparted with the interfacial activities, say, neither highly hydrophobic nor highly hydrophilic. These interfacial active nanoparticles, similar to surfactants, prefer to attach at the water/oil interface, leading to randomly close-packed monolayer films [1]. Besides, they are also able to stabilize emulsion and thus to form capsules with nanometer-controlled permeability [2]. In the case of aqueous nanoparticles with charged surfaces, lowering surface charge density may increase the surface hydrophobicity, rendering the particles interfacial active. In this scenario, we demonstrated a reversible way to use pH to tune the surface wettability of nanoparticles from highly hydrophilic to interfacial active [3]. Annealing of metallic nanoparticles self-assembling at the water/oil interface also led to freestanding films of the nanoparticle monolayers over areas as large as 1 cm$^2$ [4]. Based on the interfacial activity of nanoparticles, we also succeeded in using water/oil interfaces as platforms to layer-by-layer grow multilayered free-standing films of different nanoparticles [5-6].

References:
STRUCTURAL CONTROL OF REVERSE MICELLES IN WATER FREE SYSTEMS

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Reverse micelles exhibit less variety of structures as they are often in spherical shape and generally water is needed to form reverse micelles in organic solvents. Despite this anticipation, we present a variety of reverse micellar structures (spherical, cylindrical and planar like) in mono-and diglycerol fatty acid esters (C_mG_1 and C_mG_2)/oil systems without water addition. The generalized indirect Fourier transformation (GIFT) analysis of the small-angle X-ray scattering (SAXS) data gives pair-distance distribution functions (PDDFs), which provide a quantitative estimation of the reverse micellar structure (shape and size).

The C_mG_1 and C_mG_2 form reverse micelles in a variety of organic solvents depending on compositions and temperatures without water addition [1,2]. A symmetrical bell shaped PDDF curve of the 5wt% C_14G_2/cyclohexane as shown in Fig.1a is a signature of spherical micelles. An asymmetry in the shape of the PDDF curve is developed, when octane replaces cyclohexane, indicating a prolate ellipsoid type of micelle. Upon increasing chain length of the oil (octane, (C_8) to tetradecane, (C_14)), a pronounced peak in the low-r regime with an extended tail to the high-r side of the PDDF curve is observed, which is a typical feature of a cylindrical micelle. The inflection point after the maximum in the PDDF curve (indicated by a broken line) semi-quantitatively measures the cross section diameter of the hydrophilic core. A clear picture of one dimensional micellar growth is seen with increasing surfactant concentration (Fig.1b). Increasing temperature induces cylinder-to-sphere type transition, which is possibly due to penetration of oil to the lipophilic chain of surfactant. The reverse micelle swells with water, which in turn results a drastic elongation in the micellar structure. Hydrophilic size of the surfactant plays a crucial role in the reverse micellar structure. In a particular solvent reducing hydrophilic size from di- to monoglycerol unexpectedly shortens the micelles.

![Fig.1](image.png)

Fig.1: (a) Pair-distance distribution functions (PDDFs) of the C_14G_2/oil systems, and (b) the same for the C_14G_2/octane at different concentrations.

References:
EFFECTIVE AQUEOUS BOUNDARY LUBRICATION BY A STUBBORN SEMI-FLUORINATED SURFACANT

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In classic boundary lubrication in air or oil media, monolayers of surfactants are anchored on the rubbing solid surfaces to reduce friction and wear, and its molecular mechanism is well understood: rubbing between the underlying substrates is largely replaced by sliding between the hydrocarbon tails of the anchored surfactant boundary layers, as the van der Waals bonds between the tails are the weakest link with respect to shear. Surfactant molecules are also ubiquitous in aqueous media and may adsorb readily onto solid surfaces to form various surface aggregates. How would they participate in the tribological process in aqueous media?

We have recently proposed that the molecular mechanism for aqueous boundary lubrication has a rather different origin \cite{1,2}. Unlike in air or oil, sliding takes places around the hydrated surfactant headgroups due to their greatly enhanced lateral mobility under water.

Here we report further measurements between two semi-fluorinated surfactant bilayers under water made with a surface force balance. Our results lend strong support to the above mechanism and also allow a critical examination of different roles that surfactant headgroups and tails play in mediating effective aqueous lubrication.

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References:
FORMATION OF POLY ElecTROlyte/LIPID COMPOSITE MULTILAYER STRUCTURES

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Hybrid systems between biological and artificial materials (e.g. polymers or polyelectrolytes) are sought, since they allow one to combine the functionality of natural molecules with a potential for tailoring the thickness and the shape of coatings. Lipids self-assembling in well ordered (bi)layers can be used to compartmentalise polyelectrolyte (PE) multilayers (PEM) structures thus allowing complex well-ordered layer structures to be obtained. PEM adsorbed on solid support were introduced as highly versatile surface coatings. Their formation is based on the layer-by-layer (LbL) deposition technique, which exploits the fact that PE adsorb onto surfaces of opposite charge and that the surface charge density is reversed by this process. Because of its versatility the technique has been extensively used to produce variety of materials with potential applications in biosensors, microelectronics, and optics.

We demonstrate formation of mixed structures which consist of PE multilayers with incorporated lipid layers made by absorption from suspensions of lipid vesicles. The build up process was monitored in situ by the use of neutron reflectometry and QCM technique.

Formation of DMPC layer with thickness of 5 nm is possible onto PEM. The behaviour is explained by the electrostatic attraction between the negatively charged PSS and the DMPC molecules. Homogeneous lipid layers are formed only at temperatures above the temperature of the main phase transition when the lipid is in fluid phase. Fine tuning of the preparation procedure allowed formation of (charge) asymmetric lipid layers. PE layers were deposited also onto these lipid layers building-up PEM/lipid bilayer/PEM charge gradient sandwich like structures.

Lipid vesicles where used as carriers of metal particles. Well ordered 2D compartments in the PEM filled with particles where prepared.
TOWARDS MAGNETIC RESPONSE OF COMPOSITE MATERIALS. NANOPARTICLE INCORPORATION INTO POLYMER MATRIX

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Fabrication of well-defined nanostructures is one of the prerequisites to obtain nanocomposite materials of desired novel functions. Complex polyelectrolyte/nanoparticle systems are promising in that area as they combine the sensitivity and response of polymers to external stimuli, e.g., polymer swelling and flexibility with stiffness of the particles resulting in interesting mechanical properties. The properties of the obtained materials depend strongly on the inter particle distances in the matrix. The internal structure of aggregates ranges from close-packed clusters to tenuous fractals, depending on the system and preparation, with consequences for the mechanical (physical) response of the samples.

In our work we have focused on the incorporation of magnetite nanoparticles onto/into polyelectrolyte multilayers (PEMs). The ordering of nanoparticles depends on the treatment of underlying polyelectrolyte films. The NP are uniformly distributed in freshly prepared samples while only highly concentrated layer of NP was formed when the PEM were temperature treated after their preparation. The observed effect is correlated to melt transitions in the PEM reported earlier.

In another set of experiments, where PEM acted as a cushion for lipid bilayer with a highly hydrophobic center, NP were “arrested” within the highly hydrophobic lipid layer and prevented from penetration into the neighboring hydrophilic PEM layers. The NPs were inserted directly into the lipid bilayer during its preparation from lipid vesicles with embedded NPs.

As neutrons are sensitive to magnetic moment of the sample i.e. moments of magnetic domains in the sample, we have studied magnetic response of magnetite-PEM composites. We found magnetic response from the samples which proves formation of materials with appropriate high concentration of magnetic nanoparticles.
INVESTIGATION OF MIXED $\beta$-CASEIN/SURFACTANT LAYERS AS STUDIED BY SEQUENTIAL AND SIMULTANEOUS ADSORPTION

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Mixed systems containing low-molecular-weight surfactants and proteins play a very important role in many technologies, such as cosmetics, food industry, coating processes, oil recovery. Proteins and surfactants follow very different adsorption mechanisms and provide also different properties to interfaces. Therefore, to understand the interactions between these two very different kinds of surface active species is very important from the aspect of stability in such colloidal systems like foams and emulsions. Using the drop profile analysis tensiometry equipped with a special coaxial capillary and a double dosing system for dispensing liquids, we studied the displacement of the pre-adsorbed random coil protein $\beta$-casein from the air/water interface by different surfactants. The sequential adsorption route of creating an interfacial layer was arranged by the coaxial double capillary. Equivalent surface layers were also formed by adsorption from a mixed protein-surfactant solution. This method also allows dilational rheological experiments at low frequencies based on harmonic oscillations of drops. The equilibrium surface tension and dilational visco-elastic properties were examined for these two ways of surface layer formation. The results suggest that the displacement of the protein from the surface by surfactant molecules is caused by the modification of the protein due to complexation. The displacement of the protein or protein/surfactant complexes from the surface is due to competition with the free surfactant molecules. Quantitative theoretical models have been derived respectively, which describe the equilibrium state as well as the dynamics of the mixed interfacial layers. The structure differences of the surface layers formed by the two different ways are caused mainly by the location where the protein/surfactant complexes are formed, in one case in the bulk (simultaneous adsorption) and in the second case only at the surface (sequential adsorption).
CALCIUM UPTAKE BY CASEIN EMBEDDED IN POLYELECTROLYTE MULTILAYER

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In recent years there has been an increased interest in intrinsically unstructured proteins (IUP), i.e., proteins that in their natural state do not adopt stable, folded structures [1]. Proteins of this type, abundant in nature, play an important role in living organisms, however, despite their function is well understood, our knowledge concerning their adsorption and selforganisation is rather limited. A characteristic feature of IUP’s is their open structure, which becomes preserved even after ligand binding. Casein is one of the most common IUP’s present in milk and its products. In aqueous solution casein is surface active and forms micellar aggregates. Single protein behaves as flexible, disordered, polyelectrolyte-like molecule, therefore, it should be easily integrated into polyelectrolyte films. Casein has ability to bind calcium ions and therefore, it can be used in biotechnology and in biomedical applications. Materials covered with casein containing films can be also applied in diary industry for the prevention of calcium deposit formation.

The aim of our work was to investigate formation of polyelectrolyte multilayer films containing α- and β-casein. Since in neutral pH casein is negatively charged (as verified by electrophoretic mobility measurements) it was either used as a polyanionic layer for the film build-up or was deposited as a single layer inside PLL/PGA multilayer film. The formation of the film was investigated by liquid cell ellipsometry and optical wave guide spectrometry. After the multilayer films were formed they were contacted with solution containing calcium ions and changes in the film was monitored. Additionally the surfaces of casein containing multilayers were analyzed with AFM and the structural changes within the film, occurring after binding of calcium ions, were monitored by FTIR. We concluded that casein embedded in the polyelectrolyte multilayer preserves its ability to bind calcium ions.

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References:
The layer-by-layer (LbL) technique has been devised by Decher [1] in the early 1990s and involves the sequential adsorption of polyanions and polycations onto any charged surface, irrespective of shape and size. Recently, it has been shown that LbL can be extended to microgels [2-4]. Contrary to hard and rigid particles, microgels are soft and porous, hence deformable and into which the adsorbed polyelectrolyte may or may not interpenetrate, depending on several parameters such as molecular weight of the polyelectrolyte but also on the mesh size of the microgel (cross-linker density). We have previously shown that the thermoresponsivity of LbL-coated smart microgels is very dependent on the location of charges within the microgel core or core-shell structure [2]. In this work, we use a negatively charged, pH-sensitive poly(N-isopropylacrylamide-co-methacrylic acid), P(NiPAM-co-MAA), microgel as template for the LbL assembly of various polyelectrolyte pairs (strong/strong, strong/weak, and weak/weak). The influence of ionic strength of the polyelectrolyte solutions as well as the molecular weight of the polyelectrolyte will be discussed. The growth of multilayers is monitored by the change in hydrodynamic radius using dynamic light scattering. We observed an “odd-even” effect on the size of the coated microgel depending on the nature of the polyelectrolyte in the outermost layer (last layer adsorbed) [4]. Adsorption of just one layer of a strong polyelectrolyte is sufficient to make the pH-sensitive microgel insensitive to pH while adsorption of just one layer of a weak polyelectrolyte retain the pH-sensitivity but with a different thermostressivity to that of the uncoated microgel [4]. With the proper choice of polyelectrolyte pairs, the size and thermostressivity behaviour can be finely tuned over a wide range. Electrophoretic measurements reveal successful charge reversal. Proof of constructive build-up of multilayers on the microgel is provided by fluorescence correlation spectroscopy performed at temperatures below and above the volume phase temperature transition (VPTT). Fluorescently-labelled polyelectrolytes, P(DADMAC-rand-DAPA-labelled rhodamine B) and poly-L-lysine labelled FITC used within the multilayer prove that successive deposition of layers on microgels do not lead to the layer underneath being stripped off [3] nor during the VPTT of the coated microgels. Scanning electron microscope and cryo-transmission electron microscope provide some visual proofs of the LbL-coated microgels.

References:
 ADSORPTION OF PROTEIN TO A LIKE CHARGED POLYELECTROLYTE BRUSH 

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Protein loaded nanoparticles are interesting for drug delivery, for protein stabilization or as catalytic particles if loaded with enzymes. A very promising way of creating these particles is protein immobilization on colloidal particles covered with a polyelectrolyte brush. Experiments have shown that at low salt concentration large amounts of bovine serum albumin (BSA) can adsorb onto particles covered with a poly(acrylic acid) (PAA) brush, that the secondary structure of the protein is almost completely retained and that the protein molecules can be released from the brush by exposure to high pH or ionic strength [1]. From this research comes also the very interesting find that BSA can also adsorb above its iso-electric point, in effect that a negatively charged protein adsorbs in a negatively charged brush.  

Two different explanations have been given to explain the phenomenon of protein to polyelectrolyte brush adsorption on the “wrong side” of the isoelectric point. The first worked out by Ballauf et al. [1], assumes that a protein is not uniformly charged. If the protein has large enough positive and negative patches, the polyelectrolyte will complex with oppositely charged patches and will evade similarly charged patches. This asymmetrical behavior could lead to a net attraction. The second explanation, the possibility of charge regulation as a driving force, was worked out by Biesheuvel et al. [2] They hypothesize that the concentration of protons inside the brush is different from that of the bulk solution due to the high local negative potential in the brush. This difference in local proton concentration might be enough to change the charge of the protein from net negative to net positive, thus leading to attraction.  

We present the results of a thorough experimental study done on the adsorption of BSA to planar polyacrylic acid brushes. Adsorption at different brush length, ionic strength and grafting density were investigated as a function of pH. The results compare well to an analytical model which includes charge regulation. We give experimental evidence that charge regulation takes place upon complexation in bulk of PAA and BSA.  

References:  
REDUCTION OF PROTEIN ADSORPTION BY COMPLEX COACERVATE CORE MICELLES ADSORBED ON SILICA AND POLYSTYRENE SURFACES

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Reduction of protein adsorption by a PEO brush formed upon adsorption of Complex Coacervate Core Micelles (C3M’s) on SiO\(_2\) and polystyrene surfaces has been studied with fixed angle optical reflectometry at various salt concentrations. The C3M’s consisted of a negatively charged polyelectrolyte, PAA\textsubscript{139}, and a neutral-positively charged block-copolymer, P\(_2\)MVPI\textsubscript{41}PEO\textsubscript{204}, mixed at stoichiometric ratio. In this study four different proteins were used: β-lactoglobulin, BSA, lysozyme, and fibrinogen. The C3M-PEO\textsubscript{204} coating is responsive to changes in pH and salt concentration and therefore can be completely removed from the surface by rinsing with concentrated salt solution (>2M NaCl) or acidic solution (pH<2). The surface can be subsequently renewed with fresh micellar solution.

C3M adsorption was higher on polystyrene than on SiO\(_2\), but subsequent reduction of protein adsorption was higher on SiO\(_2\). Upon increase of salt concentration from 5 to 100 mM NaCl adsorption of all four proteins on SiO\(_2\) was reduced by more than 90%. Reduction on polystyrene was less. This might be due to the fact that affinity to the hydrophobic polystyrene surface is stronger for the PEO corona chains than for the coacervate core polyelectrolytes, and probably upon adsorption of C3M’s a brush layer did not fully develop. Our results also suggest that the charge composition at which stable C3M’s are formed in bulk is not optimal for creating an effective coating on charged surfaces. We suggest that better results on charged hydrophilic surfaces can be obtained when micelles carry an excess of charge opposite to the charge of the native surface.
SECONDARY STRUCTURE OF PROTEINS EMBEDDED IN LAYERS OF TETHERED POLYELECTROLYTES

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The immobilization of enzymes and other biomolecules at planar or curved interfaces is an issue of central importance in biotechnology. Suitable supports should provide retention of the biological function of the proteins while leaching out of the biomolecules is to be avoided. Recently, we showed that large amounts of proteins such as bovine serum albumin (BSA) or ribonuclease A can be embedded in spherical polyelectrolyte brushes (SPB) by direct adsorption of the protein from solution [1,2]. The SPB consist of polystyrene spheres of 100 nm diameter onto which linear polyelectrolyte chains such as poly(acrylic acid) or poly(styrene sulfonate) are densely grafted. Virtually no adsorption takes place onto the spherical polyelectrolyte brushes at high ionic strength and thus the proteins can be released again in a controlled fashion by raising the ionic strength [2]. The secondary structure of the adsorbed protein was investigated by Fourier transform infrared spectroscopy in transmission mode [3]. Infrared spectroscopy is used to overcome the problem of the strong scattering of visible light because this method can be used in optically turbid media as well. The \( \alpha \)-helix and \( \beta \)-sheet content of the proteins was widely retained in the adsorbed state. Only in the case of BSA interacting with poly(styrene sulfonate) brushes a slight loss of \( \alpha \)-helix structure was observed. Infrared spectroscopy was also applied to study the thermal unfolding of RNase A embedded into the SPB [4]. Since the interaction of SPB and protein can be controlled by the ionic strength, additional experiments were performed to release the adsorbed protein. The amount of released protein was quantified and was found to be strongly dependent on the kind of protein and brush used [3]. The secondary structure of the released proteins was studied as well. Full preservation of the native secondary structure was found. Moreover, the activity of immobilized enzymes is preserved as well [5]. All results obtained so far underscore that SPB allow immobilizing proteins without impeding their biological activity.

References:
TUNING THE ADHESION OF COLLOIDAL PARTICLES BY POTENTIOSTATIC CONTROL

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The adhesion of colloidal particles to solid surfaces represents a ubiquitous phenomenon in many industrial or natural processes. Despite the increased interest in electrowetting during the last years, only little attention has been paid to the applicability of this approach in order to tune the adhesion of colloidal particles. In this study we determine the changes in adhesion between a colloidal particle and an electrode modified by a self-assembled monolayer (SAM) as function of the applied potential. The adhesion forces are measured by atomic force microscopy. The differences in the pull-off forces were not only determined in function of the applied potential but also for different surface terminations of the SAM as well as for bare and surface modified silica particles as colloidal probes. The measured adhesion forces are evaluated quantitatively and the different mechanisms contributing to the observed adhesion forces are discussed. These mechanisms include the variation of the interfacial tension according to the Lippmann equation as and long-range forces of electrostatic origin. The later can be determined from the force profiles upon approach [1]. Furthermore, for a quantitative description the surface roughness has to be taken into account. We propose various strategies to optimize this approach for different applications such as nanomanipulation.

Fig. 1. Schematic representation of the experimental set up (a) and an example for the dependence of the pull-forces from the applied potential for an electrode modified by an OH-terminated self-assembled monolayer (b) with the corresponding distribution of the pull-off forces (c).

References:
RAPID STRUCTURE ANALYSIS OF THIN LIPID-PROTEIN FILMS BY HOME-LABORATORY GISAXS AND X-RAY REFLECTOMETRY

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Rapid grazing-incidence SAXS (GISAXS) and X-ray reflectometry techniques are gaining importance as analytical tools in the pursuit of building nanoarchitected films on solid supports. With the recent availability of highly brilliant point-microfocus laboratory X-ray small-angle systems and efficient 2-D semiconductor pixel detectors, these techniques can be moved from the customary synchrotron beam-lines to the routine home laboratory. We demonstrate that both, the measurement of 2-D GISAXS patterns of lipid-protein films as well as the thickness determination of the thin-film support structure, e.g. metal layers on glass or silica surfaces in the range of 1 - 100 nm, can be performed within minutes. We present results from comparative synchrotron and home-laboratory experiments, respectively, on membrane-mimetic surface nanostructures, such as phospholipid and lipid/peptide structures. The results show that these techniques are highly practical in membrane-activity screening of drugs and in the characterization of the structural transformations involved.
SUM-FREQUENCY SPECTROSCOPY OF SINGLE STRANDED DNA MONOLAYERS

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A greater understanding of the organization and orientation of single-stranded DNA (ssDNA) immobilized on surfaces is essential for optimizing and further developing the technology based on oligonucleotide binding. Currently, spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), and near edge x-ray absorption fine structure (NEXAFS) are most often used to characterize films of ssDNA. Here we show that the technique of Sum-Frequency Generation (SFG) spectroscopy can be used to detect in-situ nucleobase orientation and conformation of ssDNA films as well as labelfree differentiation between films of different bases. Also hybridization phenomena can be directly characterized in-situ.

In SFG, a visible and an infrared beam coincide in time and space at an interface, generating a signal which travels at the sum-frequency of the two incident beams. When the infrared beam is tuned through a resonant mode of absorbed molecules, the sum-frequency signal is resonantly enhanced. An SFG signal is only generated in a non-centrosymmetric environment, resulting in the suppression of isotropic bulk signal and making this technique inherently surface specific. Being an all-optical technique, it is also non-invasive and requires no special conditions such as a vacuum. These features make SFG potentially useful for in-situ investigations of biological relevant systems, since its application to submerged interfaces depends solely on their accessibility to light. However, to date, most SFG studies have only been performed in the CH and OH stretching vibration regions, due to the difficulties of working with a table top laser system at lower wavenumbers (e.g. amide I and fingerprint region) most relevant to biological applications. Here we present the first report of in-situ SFG spectra for ssDNA films of different bases in the CH stretch, amide I and fingerprint region obtained by our femtosecond broadband sum-frequency spectrometer.
CHARGE INVERSION IN BIOLOGICAL AND BIOMIMETIC MEMBRANES: ELECTROSTATIC BINDING OF DIVALENT CATIONS

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The electrostatic properties of phospholipid membranes in contact with electrolyte are of fundamental importance in many biological processes such as signalling or protein binding. The bare electrostatic charge of biological or biomimetic membranes is typically negative since membrane phospholipids are either negatively charged or neutral. However, membranes containing domains of some specific membrane lipids have a surprisingly high affinity for binding certain cations to the membrane, even exhibiting the phenomenon of charge inversion (a total number of bound counterion charges that exceeds the negative membrane charge [1]). For example, membrane domains of phosphatidic acid (a key phospholipid involved for example in signal transduction) experience drastic lateral reorganization and charge inversion when divalent cations reach micromolar concentrations (a typical situation in biological signalling) [2-4]. On the other hand, biomimetic membranes with the same charge density but made of different phospholipids do not experience charge inversion.

The experimental results can be easily interpreted by invoking a new mechanism of electrostatic correlations (electrostatic complexation or bjerrum pairing at the interface) capable of producing complex specific phenomena such as specific ion-surface interactions or counterion-proton release competition [3]. We have developed a detailed description of this new mechanism by comparing new X-ray measurements of divalent cation distributions near phospholipid membranes with computer simulations developed with atomic resolution [4]. Also, our statistical thermodynamics description of the electrostatic complexation mechanism allows us to predict the binding constants of counterions to specific interfaces and to predict the onset of charge inversion for different combinations of electrolyte solutions and biological or biomimetic interfaces.

We conclude with a discussion of the implications of our results in the context of recent experimental studies in model systems and in real cells.

References:
FUSİON AND FİSİON OF FLUİD AMPHİPHİLİC BİLAYERS:
A KİNETİC STUDY

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The fusion and fission of fluid amphiphilic bilayers is a key process in biology, occurring both on the cellular and subcellular level. In a model system of excess water (D\textsubscript{2}O), oil (n-decane) and nonionic surfactant (C\textsubscript{12}E\textsubscript{5}) the kinetics and mechanisms of transitions between two phase types of extended amphiphilic bilayers, i.e. the lamellar and sponge phase, are investigated (see Figure 1a). An abrupt change in temperature is used to initiate these phase transitions. The isotropic sponge or L\textsubscript{3}-phase consist of a continuous membrane of multiply connected passages extending in three dimensions, while the anisotropic lamellar or L\textsubscript{α}-phase is composed of stacks of bilayer sheets. Thus the L\textsubscript{3}-to-L\textsubscript{α} transition involves passage annihilation/bilayer fission, while passage formation/bilayer fusion marks the reverse case. By employing time resolved \(^{2}\text{H}-\text{NMR spectroscopy and SANS, it is found that these transitions occur through essentially different mechanisms: nucleation and growth in the case of the L\textsubscript{3}-to-L\textsubscript{α} transition (see Figure 1b,c) and the formation of locally uncorrelated passages in the reverse case [1,2]. The kinetics of the L\textsubscript{3}-to-L\textsubscript{α} transition (successfully described by the Avrami model) are strongly dependent on the change in temperature, the bilayer volume fraction, and viscosity, and they are slow (ca. 300-4000s) when compared to the reverse transition (ca. 600s). Although initial (<200s) passage formation occurs very quickly in the fast L\textsubscript{α}-to-L\textsubscript{3} transition, it appears that this slows considerably once a critical passage density is attained. Evidence suggests that disruption of long range lamellar order might also be a rate limiting process in this case. In the L\textsubscript{3}-to-L\textsubscript{α} transition, it is found that lamellar nuclei form at considerably higher bilayer volume fraction, than the equilibrium value. This can inhibit progressive nucleation at an advanced point in time. This work represents the first systematic study on nucleation and growth phenomena in a microemulsion-type system. The results form the basis for improving the theoretical description of bilayer fusion and fission.

Fig. 1. a) schematic illustration of the lamellar (L\textsubscript{α}) and sponge (L\textsubscript{3}) phase structures which form after thermally induced phase transitions; b) typical evolution of \(^{2}\text{H}-\text{NMR spectra for a L\textsubscript{3} to L\textsubscript{α} transition; c) spectra of the left in superposition. Two isosbestic points are clearly visible.}

References:
STRUCTURES OF AMPHIPHILIC ROMP BLOCK COPOLYMERS IN SOLUTION AND IN FILMS

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The self-assembly of block copolymers to form well ordered structures is of great interest for the design of hierarchical materials. In this contribution, the morphologies and properties of well-defined block copolymers with narrow molecular weight distributions prepared by ring opening metathesis polymerization are studied. Two series of amphiphilic AB-block copolymers poly-[(endo, exo [2.2.1] bicyclo - hept- 5 – ene - 2,3 - dicarboxyclic acid dimethylester) – b - (endo,exo [2.2.1] bicyclo-hept-5-ene-2,3-dicarboxyclic acid)] of different block ratios and lengths were investigated. The structures formed were investigated in solution [1], in thick films [2] and in thin films using dynamic light scattering, small angle x-ray scattering, grazing incidence small angle x-ray scattering, and electron microscopy. A variety of different structures were found. The structures are similar to the ones expected for block copolymers in equilibrium, although annealing is not possible for the polymers studied due to thermal instability. Lamellae, hexagonally packed cylinders and globules with liquid like arrangement were observed. Such structures were seen in thick and in thin films and can be correlated to the micellar structures in solution.

References:
INFLUENCE OF TEMPERATURE AND pH ON THIN TERMORESPONSIVE PNIPAM FILMS

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During the last decades microgels made of N-isopropylacrylamide (NIPAM) have attracted much interest and were studied by several techniques like microscopy and light scattering [1]. These polymer particles show thermoresponsive behaviour and can therefore be classified as “smart” materials. By copolymerisation with organic acids [2] such as acrylic acid (AAc) the temperature of the volume phase transition as well as the swelling ratio can be influenced. Moreover charged copolymers are sensitive to changes in pH and ionic strength. Depending on the way of preparation one can achieve particles with rather low polydispersities which makes them more interesting for applications like surface coatings and sensor design [3]. The aim of our work is to study the behaviour of microgel particles at surfaces.

Two types of microgels were synthesised: PNIPAM microgels and PNIPAM microgels with 5\% content of acrylic acid (PNIPAM-co-AAc). The microgels were prepared via emulsion polymerization in water without using surfactants with 5\% content of crosslinker N,N-methylenbisacrylamid (BIS). The films were prepared on silicon wafers by spin coating and dip coating methods. The surface of silicon wafers were coated by polyethylenimin (PEI). Film characterisation has been done using Atomic Force Microscopy (AFM) and ellipsometry. While AFM allows obtaining information about the particle size and arrangement [4], ellipsometry focuses on the overall film thickness [4]. The film structure depends on the methods of film preparations, concentration and pH of microgel dispersions.

In order to study the films under various conditions such as temperature and solvent composition we employed liquid cells which allowed studying the surfaces under solution. The results show that the way of preparation and external stimuli like pH and temperature influences strongly the film structure.

References:
LITHOGRAPHY-FREE APPROACHES TO PATTERNED SURFACES BASED ON WRINKLING

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Surfaces that are structured on the micron or sub-micron-scale play an increasingly important role as building blocks for devices in areas as diverse as photonics, catalysis, sensorics or biotechnology. For these applications, surface architectures consisting of patterned surface properties (wettability, surface charge density, chemical or biological functionality) and/or patterned topography are sought for. While patterning can be achieved using modern lithography techniques, this approach is rather expensive and difficult to upscale to areas of macroscopic dimensions. In contrast, controlling mechanical instabilities like wrinkling can be exploited for creating patterns with considerably lower effort.

Wrinkles develop (for example) if a soft substrate covered by a hard film is exposed to strain or if such a substrate-film combination is built up in a strained state and subsequently relaxed. In the latter case, permanent topographical patterns with periodicities between fractions of a micron and many microns are formed. Wrinkle patterns are highly regular and the lateral dimensions of the substrate can be macroscopic without loss of control. Apart from topographical patterning, the approach can be used for achieving chemical contrast as wrinkled surfaces can be subsequently employed for printing processes or controlled deposition of colloidal particles [1]. We discuss recent developments and perspectives of the approach.

References:
DIRECT VISUALISATION OF A SELF-ORGANISED MULTILAYER FILM OF LOW $T_g$ DIBLOCK COPOLYMER MICELLES

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The first in situ proof of the presence of true micelle structure within alternating layers of a self-assembled cationic and anionic diblock copolymer micelle-micelle multilayer film on a silica substrate is presented using atomic force microscopy.[1] Assembled at pH 9 in aqueous solution, the ‘cationic corona’ micelles used in the multilayer were 10% statistically quaternised poly (2-(dimethylamino) ethyl methacrylate) -b-poly (2-(diethylamino) ethyl methacrylate) (10qPDMA-b-PDEA) and the ‘anionic corona’ micelles used were poly(methacrylic acid)-b-poly(2-(diethylamino)ethyl methacrylate), (PMAA-b-PDEA).

The presence of micelles is unambiguously confirmed within each layer. Moreover, interaction force curves recorded normal to each layer indicate substantial adhesive forces between adjacent layers. The electrostatic nature of this interaction provides direct evidence for the electrostatic mode of self-assembly. Unlike in previous reports of micelle-micelle multilayers, the diblock copolymers used in this study have sub-ambient $T_g$ values, thus the micelles are soft and may well undergo some exchange with unimers in bulk solution during the construction of the multilayer film. The high water content and stimulus-responsive nature of such multilayer films together with their mechanical resilience augur well for their future application.

References:
ORGANIZATION OF MAGNETIC/NOBLE METAL HETEROSTRUCTURES BY AN APPLIED EXTERNAL MAGNETIC FIELD

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During the last years, metallic nanoparticles were the subject of a large number of studies due to their extraordinary physical and chemical properties [1,2]. Thereby, their electric and optical properties highly depend on the specific particle size, shape, and surrounding environment. Especially, gold nanoparticles are in the focus of interest because of their potential use in microelectronic, optical, and biomedical applications. The capability to synthesize nanoparticles with a magnetic component will help to improve the formation of organized structures by applying different magnetic fields to such nanoparticles which have different magnetic properties. This work shows the synthesis of novel bimetallic-magnetic nanoparticles being formed by a noble metal and a magnetic component. Furthermore, the possibility to control both, size and shape of the both components is demonstrated. FePt nanoparticles, as the magnetic component, were first synthesized in an organic medium, subsequently transferred into water, and finally used as a seed for the reduction of gold salt. This procedure results into Au-FePt nanocomposites. Moreover, these heterostructures were organized into lines by the influence of an applied external magnetic field. Characterization was done by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM), and UV-vis spectroscopy. The objective of the presented project is concerned with the optimization of the wet-chemical synthesis of novel metal-magnetic heterostructures, to obtain narrow size and shape distributions of the produced magnetic nanocomposites, and to tailor their optical and magnetic functionalities.

References:
POLYELECTROLYTE-STABILIZED NANOPARTICLES REDISPERSED FROM A MICROEMULSION TEMPLATE PHASE

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Polyelectrolyte-modified microemulsions were formed by incorporating homo- and copolymers of diallyldimethylammonium chloride (DADMAC) into water-in-oil microemulsions. The resulting isotropic solutions were characterized by means of \(^1\)H NMR self-diffusion measurements, conductometric, calorimetric, and rheological measurements. The droplet structure was visualized by means of ultra-high resolution cryo scanning electron microscopy (Cryo-SEM).

Our results show that poly(diallyldimethylammonium chloride) (PDADMAC) can be incorporated into the individual water droplets of a water-in-oil microemulsion (L2 phase) by using different surfactant components, i.e. the anionic sodium dodecylsulfate (SDS) or the zwitterionic 3-(N,N-dimethyldodecylammonio)propanesulfonate (SB) [1].

The oil component can be a long chain alcohol, like heptanol, or a mixture of pentanol and toluene. When the molar mass of the PDADMAC is low, that means the radius of gyration of the polymer is smaller than the droplet size, polyelectrolyte-filled microemulsions can be produced up to a polymer concentration of 30% by weight of the polyelectrolyte in the aqueous phase.

It is also possible to incorporate copolymers of DADMAC with maleamic acid (PALH) or maleamic acid derivatives with butyl (PALBu) or octyl (PALOc) side chains [2]. The polyelectrolyte-filled w/o microemulsions can be used then as a template phase for the formation of nanoparticles. Inside the water droplets one can produce bariumsulfate, magnetite, hydroxylapatite, cadmiumsulfide or zinksulfide particles with diameter smaller than 20 nm. The polyelectrolytes can mask the surfactant head groups and can control the particle growing process inside the water droplets.

During the following solvent evaporation process the polyelectrolytes can stabilize the nanoparticles, and therefore BaSO\(_4\) nanoparticles with mean particle dimensions of 6 nm, ZnS nanoparticles of about 5 nm, and magnetite nanoparticles of about 17 nm can be redispersed in water.

References:
FABRICATION OF ANISOTROPIC MICROPARTICLES AND MICROCAPSULES

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A novel method for fabrication of anisotropic particles of non-spherical shape based on oil-in-water emulsion templates embedded in a gelled aqueous phase. We also extended this technique for fabrication of anisotropic particles of non-spherical shape based on oil-in-water emulsion templates embedded in a gelled aqueous phase. The gelled emulsion was stretched or compressed macroscopically inducing a local deformation of the emulsion drops. After UV-polymerization of the oil phase, non-spherical anisotropic microparticles of various aspect ratios have been produced. The effect of different macroscopic deformation ratios on the particle shapes has been studied using optical and electron microscopy techniques. The use of this method has been extended to magnetic Janus particles. Possible applications include photonic crystals with novel symmetries, colloidal substitutes for liquid crystals and water-based electrorheological fluids. We also report a novel, scaled-down “papier mache” approach to the synthesis of anisotropic microcapsules, in which nano-cotton fibres and polyelectrolytes are used to template calcium carbonate microcrystals with needle-like and rhombohedral morphologies. This technique provides a unique route to producing anisotropic capsules whose morphologies perfectly mirror the shape and size of the template. Further, we demonstrate that this can be achieved through deposition of a single composite layer of nano-cotton fibres and an oppositely charged polyelectrolyte on the chosen template. We also present a simple technique for filling of sporopollenin microcapsules with nanoparticles and insoluble salts by using a chemical reaction or a precipitation process that generates the encapsulated compounds inside the sporopollenin shell. We demonstrate the method by producing magnetic sporopollenin (loaded with magnetite nanoparticles), and sporopollenin filled with calcium phosphate and organic salts of low solubility (see Fig. 1.).

Fig.1.
SYNTHESIS, CHARACTERISTICS AND POTENTIAL APPLICATION OF COPPER-SILVER CORE-SHELL NANOPARTICLES

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The interest to metallic nanoparticles (NP) is driven by the possibility to obtain advanced materials with unique properties (e.g., optical, electronic, magnetic, catalytic), which depend on their chemical composition, size and morphology. The most widely studied nanoparticles are those of noble metals such as Au, Ag, Pt, Pd etc. The main difficulty at the use of non-noble metals arises from their instability toward oxidation, and to be of practical importance, such nanoparticles should be protected against oxidation at ambient conditions. Solution of this problem will enable the use of non-noble metals instead of Au and Ag in electronic and optoelectronic devices. For example, high electric conductivity and low price of copper make its NPs very promising material for fabrication of conductive coatings.

We developed a new procedure for preparation of Cu NPs, stable to oxidation and aggregation at ambient conditions with the use of two-steps approach: synthesis of Cu NPs in the presence of catalytic amounts of Ag or Au NP followed by their protection with a thin layer of non-oxidizable metal, silver (Cu-Ag core-shell NPs, Cu@Ag NPs) by transmetalation reaction.

The synthesized Cu and Cu@Ag NPs were characterized and their core-shell morphology was proved by UV-Vis spectroscopy, XRD, Dynamic Light Scattering (DLS), High Resolution SEM and TEM, STEM, EDS (energy dispersive spectra), and X-Ray Photoelectron Spectroscopy. The average size of synthesized Cu@Ag NPs according to DLS, HR-SEM and HR-TEM was found to be 40-50 nm with a silver shell thickness of few nanometers. Cu@Ag NPs were shown to be stable to oxidation at ambient conditions for at least 2 months.

Potential application of synthesized dispersions as inks for non-contact digital printing of conductive patterns on various substrates was demonstrated.
FORMATION OF ORGANIC NANOPARTICLES FROM NANOEMULSIONS

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Nanoparticles can be obtained from confined nanometer structures, such as: micelles, liquid crystals and nano-emulsion droplets. The oil droplets of nano-emulsions can be used as “nanoreactors” in which precipitation or polymerization occur, resulting in polymeric nanoparticles.

Preparation of nanoparticles from emulsions usually requires high input of mechanical energy, by using, for example, high-pressure homogenizers or by applying high ultrasound energy. Here we report on preparation of nanoparticles prepared from nanoemulsions prepared by inversion techniques.

Poly lauryl acrylate nanoparticles were prepared from nanoemulsions prepared by the PIT method, while the oil phase is composed of water immiscible monomer, lauryl acrylate. The emulsions were prepared using Brij 96 and a combination of Brij 96 and Brij 92 at various ratios (HLB) and concentrations. The effect of the surfactants’ HLB and concentration on the emulsions’ droplet/particle size was evaluated. The nanoparticles were characterized by using: Cryo-TEM and dynamic light scattering. The nanoparticles contained, in some cases, a crosslinking agent in addition to the monomer.

Pyrene, a probe for microviscosity, was encapsulated in these particles and was used to study the changes in microviscosity after the polymerization of the nanodroplets.

The emulsion-inversion method was also applied to obtain nanocapsules, by interfacial polymerization of nanoemulsions.
DIFFERENT TYPES OF ZINC-DECORATED NANOPARTICLES FOR PROTEIN BINDING AND CONTROLLED RELEASE

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The aim of this study was to bind reversibly histidine-rich proteins to the surface of selected nanoparticles via coordinative bonding using Zn ions as the anchoring points. As a model histidine-rich protein, bovine serum albumin (BSA) was used. The release of BSA bound onto Zn-decorated nanoparticles was analysed by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). We demonstrate that the bonding of BSA on such modified nanoparticles is highly reversible and can be controlled by appropriate change of external conditions such as pH decrease or presence/supply of other chelating compound. When a biologically active agent is bound to a substrate (nanoparticle), it is less prone to enzymatic degradation and, thus, more stable. This increases the efficiency, prevents losses of active agent and exposure of the human organism to a possible toxic agent. The nanoparticles investigated in this work could be interesting for binding of proteins that are cytotoxic in higher doses, as in the case of analogues of tumor necrosis factor alpha (TNF-alpha).

Fig. 1. Schematics of BSA - zinc - silica-coated maghemite nanoparticles prepared by layer by layer technique.
INTERNAL STRUCTURE AND CRITICAL BEHAVIOUR OF THERMORESPONSIVE CORE-SHELL MICROGELS AS SEEN BY SMALL ANGLE NEUTRON SCATTERING

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Thermoresponsive core-shell microgels were synthesized by a simple surfactant-free radical emulsion polymerization using N-isopropylacrylamide (NIPAM) as monomer and inorganic nanoparticles as core materials [1,2]. The crosslinker density (N,N’-methylenebisacrylamide) of the poly-NIPAM shell was 5%. The overall size of such particles was determined from dynamic light scattering as well as imaging techniques like electron microscopy and atomic force microscopy. These real-space techniques were additionally used to verify the core-shell structure.

![AFM image of a Silica-poly-NIPAM core-shell microgel.](image1)

Fig. 1: Left: AFM image of a Silica-poly-NIPAM core-shell microgel. The particle in the center is coreless. Middle: SANS profiles of a core-shell microgel with silica cores. Right: Scaling-plot for the correlation length $\xi$. The obtained slope from a linear fit has a value of -0.67 and is close to the predicted value from the 3D Ising model (-0.625).

In order to characterize the internal structure of the polymer part of these smart hybrids we employed small angle neutron scattering (SANS), which provides the correlation length $\xi$ of the polymer network. By measuring SANS profiles at different temperatures in the vicinity of the volume phase transition of the poly-NIPAM shell the evolution of $\xi$ as a function of temperature was investigated. In good agreement to theoretical predictions we found a scaling behavior with a scaling exponent close to 0.625, which corresponds to the 3D Ising prediction for this kind of collapsing network. The presented hybrid microgels are possible candidates for many applications such as sensor design and photonic crystals. Hence, a characterization with regard to the swelling behavior and the internal structure is essential. In addition to the investigation of the scaling behavior this contribution aims to show that the core particles have no influence on the swelling and the morphology of the polymer gel, at least if a certain core size range is not exceeded.

References:
Responsive polymer microgels can be employed for the preparation of stimuli-sensitive emulsions. In this contribution we will report on the properties of such particles at oil/water interfaces and as stabilizer for emulsions. The microgels we used are based on crosslinked copolymers including N-isopropylacrylamide and methacrylic acid. The particles were characterized by means of light scattering, titration as well as electrophoretic mobility. As it turns out, synthesis conditions of such microgels and the work up procedure following have a significant impact on the properties of the microgel stabilized emulsions.

These particles can be utilized to stabilize emulsions with oils of very different polarity. As the microgels themselves are pH- and temperature-sensitive, the emulsion stability responses to changes in pH and/or temperature. Those emulsions can be broken and the microgel can be reused to act as a stabilizer once again. The droplet size distribution of the emulsions is determined and the data provide information on the emulsion stability as well as on the influence of preparation techniques on the emulsion composition.

The interfacial activity of stimuli-sensitive microgels was investigated by means of the pendant drop technique. Surprisingly it turned out that microgels reduce the interfacial tension even under pH conditions in which no stable emulsions can be prepared. To explain this contradiction we will present data from interfacial rheology measurements, and cryogenic scanning electron microscopy, giving new insights in the mechanism of stabilisation.
VESICLE GELS AS TEMPLATES IN THE FORMATION OF MESOPOROUS MATERIALS

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The synthesis of mesoporous inorganic materials obtained via templating self-organised amphiphilic systems is a very active topic in colloidal and material science. As such templates various micellar structures or lyotropic phases may be employed. In this work vesicle gels of ionic surfactants and a co-surfactant were studied with respect to their ability to solubilise appropriate precursors for inorganic template synthesis. Depending on the content of ionic surfactant and co-surfactant they are able to solubilise large amounts of precursors where the solubility depends on the total concentration and composition of the surfactant mixture. As the vesicle gels can be formed by a simple mixing process of the starting components the whole templating reaction can be done in a homogeneous system in which vesicle formation and hydrolysis of the inorganic precursor take place in parallel. In order to follow the structural changes of the combined system surfactant/inorganic material as a function of time SANS experiments were applied. This allows in principle to follow how the typical scattering pattern of the vesicle gels evolves and if it is retained during the templating process. Investigations by SAXS, N₂-Adsorption, and scanning electron microscopy (SEM) show that upon calcination interesting new mesoporous oxides (silicate or titanate) are formed, in which the gel structure is retained.
O98

POLYELECTROLYTE MULTILAYERS USED TO DESIGN MECHANICALLY RESPONSIVE FILMS

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The alternate deposition of polyanions and polycations on a solid surface leads to the formation of films whose thicknesses grow with the number of deposition steps. These films are called polyelectrolyte multilayers [1] can be used to build architectures that are stimuli responsive. We will present two examples of stimuli responsive films. Both films are constituted of polyelectrolyte multilayers deposited on silicone sheets. One example concerns a film whose hydrophobicity can be changed reversibly by stretching [2]. This film is constituted of (PAH-Nafion)n-(PAH-PAA)m multilayer (PAH : poly(allylamine); PAA : poly(acrylic acid)) that is deposited on a plasma treated silicone sheet. The contact angle of water varies reversible from 60° to 100° back and forth under stretching and coming back to the non stretched state. A second example concerns a film composed of two compartments separated by a barrier which can be opened and closed reversibly by simple stretching [3,4]. All these constituents are made of polyelectrolytes multilayers. Once the barrier is open, polyelectrolytes can diffuse from one compartment to the next. These systems should also allow protein diffusion from one compartment to the next. We will also present preliminary results on films that allow to modulate a chemical reaction by simple stretching of a functionalized multilayer film.

References:
VESICLE-CONTAINING MULTILAYERED POLYELECTROLYTE FILMS MADE BY THE LBL TECHNIQUE. POTENTIAL FOR IMPLANT BIOCOATING.

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Integration of small vesicles (phospholipid or polymer) into soft gel-like polyelectrolyte films was studied. The film was constructed using the layer-by-layer technique [1,2] by alternating adsorption of hyaluronic acid (HA) and polylysine (PLL), yielding micrometer-sized architecture with controlled thickness and common formula (HA/PLL)x [3]. Design of the composite film is developed. Morphology and structure of the formed films as well as vesicle stability in both solution and film-entrapped state were investigated. Vesicle stability is sufficiently enhanced by polymer surface coating [4-6]. The ways to control a release of vesicle cargo upon external stimuli were proposed and discussed. The composite film is promising implant biocoating for controlled drug delivery. Local delivery of drugs (antibiotics, growth factors, etc) between an implant and surrounding tissue can strongly enhance drug efficiency in order to reduce biomaterial-associated complications.

References:
COLLOIDAL CRYSTALS – DEAF LİMS AND GOLDEN CROİSSANTS

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In this contribution we will present comprehensive results on the phononic properties of colloidal crystals and span the bridge to nanostructured materials by colloidal crystal templating. The interaction of light with colloidal or “photonic” crystals has been studied to a great extent, the generation of phononic bandgaps, however, is still far less understood [1]. With Brillouin Light Scattering (BLS) we were able to demonstrate the existence of two distinct phononic bandgaps in a colloidal crystal. Rational film design with disorder allowed us to selectively close one bandgap, precisely the Bragg gap, which originates from the fcc order.

Furthermore, monolayers of colloidal particles have been widely used for surface structuring in the nanometer regime. A bottleneck for widespread applications was the availability of monolayers on a large, i.e. square centimetre, scale. We therefore developed a new and simple technique, which allows fabricating large area monolayers. These monolayers were further on used to template nanostructures like crescent shaped gold nanoparticles [2]. Besides the advantage of high nanoparticle density and orientation, this method also allows us to precisely tune the interparticle distance.

References:
ELABORATION OF PHOTONIC COLLOIDAL CRYSTALS WITH A WELL DEFINED ARCHITECTURE

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Colloidal crystals are expected to have applications in optical devices such as photonic band gap crystals. For these applications, it is critical to fabricate a high-quality colloidal crystal with a controllable organization. We present here the fabrication by the Langmuir-Blodgett technique of three-dimensional colloidal crystals containing planar defects of various types. We have investigated the structure-optical properties relationship of these materials by combining Scanning Electron Microscopy (SEM) and Near-Infrared (NIR) spectroscopy experiments.

We show that the defect state position in the stop band varies periodically with the value of the ratio of the diameter of the colloids of the lower and upper opals to the size of the particles of the defect layer. Moreover, both the wavelength and the magnitude of the pass band are found to continuously vary with the position (i.e. altitude) of the defect layer inside the material. We demonstrate that the incorporation of one to four periodically distributed planar defects in colloidal crystals induces the opening of new gaps and bands in the original photonic band structure. These experimental results were successfully simulated and the results of the simulations are presented and discussed.

References:
3D-ORDERED ARRAYS FROM POLYMERIC PARTICLES: PREPARATION AND INFILTRATION

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Nowadays monodisperse polymeric particles as functional building blocks of hierarchic nanostructured materials are of great interest. Particularly, such particles are capable of self-assembling into 3D-ordered arrays with periodically modulated refractive index. If the particles have submicron diameter their arrays demonstrate photonic band gap (PBG) in the spectral range of visible or near IR light.

To prepare polymeric particles having high assembling capability into perfect 3D lattices, emulsion emulsifier-free copolymerization of styrene with hydrophilic functional comonomers, such as methacrylic acid [1] or N-vinylformamide, was applied. Properties of particle surface enriched with carboxylic or amino groups could be easily regulated by pH and the ionic strength of dispersion media during polymerization step as well as under self-assembling. Thin 3D-ordered films of the particles were fabricated on glass slides from their dispersions in water or ethanol. SEM and scanning spectroscopy were applied to test film structure and photonic crystalline features. The Bragg reflection spectra obtained for polarized light at different angles of incidence were well simulated in the theoretical calculations [2].

The infiltration of polar solvents into interparticle voids of 3D-ordered films was also studied. The more hydrophilic particle surface ensured both filling 3D-ordered arrays and their adhesion to glass substrates. Due to rather low dielectric contrast in the films prepared, we were able to observe, firstly for 3D photonic crystals, an analogue of the Brewster effect corresponding to the PBG inhibition for p-polarized light at a certain angle of incidence. The infiltration of Ti(OBu)₄ solutions into interparticle voids followed by hydrolysis and crystallization of TiO₂ simultaneously with removal of polymeric template under heating allows preparing inverse photonic crystals with modified photonic crystalline features.

References:
INCORPORATION OF ORGANIC MONOMERS WITHIN A CARBON MATRIX VIA ONE STEP HYDROTHERMAL CARBONIZATION

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Here, we report a procedure in which organic monomers can be replaced by the controlled decomposition products of carbohydrates, which can be copolymerised or undergo cycloaddition reaction with functional co-monomers to give a new type of latexes or polymer dispersions. These latexes consist of renewable raw materials, having a low cost base and expanding the emulsion polymers to carbonaceous materials. This present synthetic strategy can be extended to various compositions of different water soluble organic monomers yielding materials that combine the surface properties of the polymers with the electric conductivity of the carbon framework.

The monomers used in this study are acrylic acid, vinylimidazole, vinlylalchool and 2-acrylamido-2methyl propane sulfonic acid. Hydrothermal carbonization of glucose [1,2] was performed in the presence of these previously mentioned monomers. The resulting materials were characterised using various methods including Boehm's titration, FT-IR, Zeta Potential, N\textsubscript{2} and H\textsubscript{2}O adsorption, SEM, TGA and solid state \textsuperscript{13}C-NMR. Morphological changes as compared to the materials obtained upon the hydrothermal carbonization of pure glucose were observed in all cases. Depending on the choice of monomers different functionalities were added to the resulting final material.

The resulting functional carbonaceous materials were successfully applied in fields such as adsorption, catalysis and electrochemistry.

This method provides a “green” solvent and surfactant free access to hydrophilic carbon/polymer composites with very good water dispersivity.

References:
COLLOIDAL TRANSPORT ON MAGNETIC GARNET FILMS

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Paramagnetic colloidal particles dispersed in water and placed above the domain walls of an uniaxial ferrimagnetic garnet film, can be transported in different location of the film when subjected to external magnetic modulations. With this strategy we realized a magnetic colloidal shift register that allowed programmable, dispersion free particle motion, separation and subsequent logical operations on the complex biological libraries transported by the particles [1-3]. Also, we studied the rich dynamics of particles externally driven through periodic pinning potentials that are made by array of magnetic bubble domains [4]. All these methods to manipulate colloidal carriers, can be used into integrated microfluidics systems, or applied in colloidal, chemical and biomolecular researchs.

References:
THE DROP SIZE IN MEMBRANE EMULSIFICATION DETERMINED FROM THE BALANCE OF CAPILLARY AND HYDRODYNAMIC FORCES

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We investigated theoretically and experimentally the production of monodisperse emulsions by means of microporous membranes. To understand the mechanism of drop detachment from a pore, theoretical calculations for the case without cross flow have been performed. The Navier-Stokes equation has been solved and the fields of velocity and pressure have been computed for the interior and exterior of oil drop, which is growing at the orifice of a pore [1]. The driving force of the drop detachment turns out to be the viscous stress due to the flow of the liquid, supplied by the pore, which feeds the growing drop. For drop detachment, it is not necessary the viscous stress to cause a violation of the force balance in the system. Instead, it is sufficient the viscous stress to produce a deformation in the drop shape, which leads to the appearance of a necking instability, in analogy with the case of pendant-drop detachment. The theoretical predictions about the dependence of the emulsion drop size on various factors (interfacial tension, applied pressure, pore size, type of emulsifier) are compared against experimental data for emulsions produced by means of Shirasu porous glass membranes [2]. The transition from unimodal to bimodal drop size distribution (Figure 1) upon increase of the transmembrane pressure can be interpreted in terms of the transition from “dripping” to “jetting” mechanisms of drop detachment (Figure 2).

Fig. 1.     Fig. 2.

References:
MICROMECHANICS OF GAS-FILLED MICROBALLOONS

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Gas filled MicroBalloons are today highly valued research subjects mainly due to their potential use in medical applications where they impose themselves as targeted drug delivery systems and contrast agents for ultrasonic imaging. Intense research has been devoted to the development of MicroBalloon systems [1]. It is extremely important to characterize their mechanical and adhesion properties as these determine the micro containers behavior in applications and in particular in theranostics (allowing both therapy and diagnostics) where the mechanical properties determine the micro containers stability and consequently the delivery triggering conditions and where the adhesion properties are the key to an effectively targeted system. To understand how mechanical properties are affected, we use a combination of the colloidal probe AFM technique and an inverted optical microscope. The deformation behaviour of individual microballoons is characterized with AFM Force Spectroscopy measurements [2]. We analyze the dependence of the profiles with microballoon radius at different temperatures (room and body temperature). Scanning Transmission X-ray Microscopy (STXM) [3] experiments made in collaboration with Dr. Rainer Finks Group proved to be very appropriate to study the microballoons. Quantitative analysis of the resulting transmission profiles allowed us to characterize the microballoons radius, wall thickness, density and air content.

References:
DIELECTRIC RESPONSE OF A SPHEROIDAL COLLOID

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An analytical theory describing the dielectric response of a charged spheroid submitted to an external oscillating electric field in an electrolyte solution is proposed. In [1], we presented an analytical theory which gives the dipolar coefficient of a dielectric sphere in an electrolyte solution subjected to an oscillating electric field. This theory (for spheres) has now been improved and thoroughly compared to the results obtained from numerical simulations (for spheres). It will be shown that agreement between the analytical and numerical theories is good for all zeta potentials, frequencies and $\kappa a \geq 1$ where $\kappa$ is the inverse of the Debye length and $a$ is the radius of the sphere. The numerical solutions are obtained by a code based on De Lacey and White's [2].

The form of the analytical solution for a sphere enables us to derive a formula for the dielectric response of a spheroid, also valid for all zeta potentials, frequencies and $\kappa a \geq 1$. The expression we find is simpler and has a more general validity than the analytical expression proposed by O’Brien and Ward [3]. Numerical solutions [4] are also available for spheroids but, like the solution of O’Brien and Ward, are only valid for very thin double layers ($\kappa a >> 1$) and zero frequency.

References:
INTERACTION FORCES BETWEEN TWO LIKE-CHARGED COLLOIDAL PARTICLES AT A LIQUID INTERFACE: ELECTRIC REPULSION vs. ELECTROCAPILLARY ATTRACTION

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Electrically charged particles at oil-water and air-water interfaces have been found to form perfect hexagonally ordered monolayers of large interparticle spacing due to the electric repulsion. Such arrays have potential optical and photo-voltaic applications. It is important to know the forces that control the interparticle spacing and the transitions observed upon compression of such monolayers. Here, we investigate the forces of interaction between two like-charged dielectric particles, which are attached to the boundary between water and nonpolar fluid: air, oil (Figure 1a). The experiments indicate that the main electrostatic effects are due to the field in the nonpolar fluid generated by charges at the particle surface [1,2]. At long distance from the particle, its electric field has dipolar character due to the image-charge effect [3]. For this reason, the particles are modelled as dipoles that are equivalent to the real system with respect to the electric force and moment. In the framework of this model, it is possible to solve exactly the Laplace equation of capillarity and to determine the shape of the water/nonpolar-fluid interface, which is affected by the electric forces (Figure 1b). Next we calculate the capillary and electric forces and moments. The results show that in addition to the direct electric repulsion between the like-charged particles, an attractive “electrocapillary” force appears owing to the deformability of the liquid interface. Depending on the particle charge, shape and wettability, the net interparticle force can be repulsive or attractive. For bigger particles (larger than 10 µm) the interference of electric and gravity induced deformations in the liquid interface gives rise to a strong “hybrid” capillary attraction that has been experimentally detected [4].

Fig. 1. a) Forces acting on like-charged particles attached to a water/nonpolar-fluid interface: $F_{ED}$ is the electrodipping force due to the image-charge effect; $F_{ER}$ is the direct electric repulsion, and $F_{EC}$ is the electrocapillary attraction. b) Calculated meniscus shape around the two charged particles; the image is magnified in vertical direction by using appropriate scaling.

References:
COLLOIDAL INTERACTION CAUSED BY SOLUTE ADSORPTION

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Bubbles in sea water are stable much longer than in fresh water, creating sea foam. The mechanism controlling the bubble coalescence has tentatively been attributed to the presence of salt in sea water. Ion-surface interaction has been shown to be very specific to the ion species [1] but it seems to be the collective ion behaviour that inhibit or permits coalescence [2], apparently due to the proposed charge segregation in the interfacial region giving rise to classical double-layer repulsion keeping the bubbles stable [3]. A generic study and manifestation of the proposed principle has been made with a model based on complicated hypernetted chain integral equations and Monte Carlo simulations studying interaction model hydrophobic interfaces in electrolytes [3]. We have now established that in the regime of low ionic concentrations and surface charge a simple numerical evaluation of the Poisson Boltzmann-equation gives results in excellent agreement with the complicated and computationally demanding techniques. Also, in the present regime we found that the pressure evaluation reduces to a simple analytic expression proportional to the potential profile between the interaction surfaces. We have taken this approach further to model OH⁻ adsorption to oily interfaces. The agreement with experimental observations crucially depends on the sensitivity of the simulation data for the profiles of the potentials of mean force used as an input for the PB-model. There is currently a contradiction between experimentalist attributing observations to adsorbed OH⁻ and theoreticians not being able to predict that. Theoretical modelling needs to be refined to capture real scenarios. This can be done by refining the evaluation of for instance the dispersion interaction using existing theories [4] but also by extending the theories to include detailed features such as non-local dielectric properties of the solvent and anisotropic corrections of the ion-surface interaction [5].

References:
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SIMULATIONS OF SOLUTIONS OF HELIX FORMING POLYMERS

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The interplay between intramolecular structure and intermolecular interactions is investigated using a simple square-well homopolymer model. Recently, it has been demonstrated [1] that isolated, square-well homopolymers can spontaneously break chiral symmetry and “freeze” into helical structures at sufficiently low temperatures. This behaviour is interesting because the square-well homopolymer itself is achiral.

Event-driven molecular dynamics simulations, combined with parallel tempering, are performed for systems of homopolymers over a range of densities. The homopolymers possess intramolecular attractions, which drive the helix formation, but interact with each other only through repulsive, excluded volume forces. We examine how these intermolecular interactions alter the temperature at which the molecules form helices, and how the handedness of the helical molecules are correlated with one another in the system. In addition, the phase behavior of the solution is investigated.

References:
NOVEL PHASES AND FRUSTRATION EFFECTS IN COLLOIDAL LIQUID CRYSTALS– A SIMULATION AND THEORETICAL STUDY

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It is now possible to engineer hard colloidal particles with a wide variety of shapes [1] so a new role of theory and simulation is to discover which shapes will show interesting and novel behaviour. Here we present simulation and theoretical results on systems of two such shapes that now can be fabricated.

Truncated hard spheres are disc-like particles which can exhibit both columnar and cubatic liquid crystalline phases [2]. In the cubatic phase, the discs are positionally disordered but exhibit a cubic orientational symmetry. We have confirmed the stability of this phase by extensive simulation. We find that this transition is predicted theoretically by a high level virial expansion, but in order to capture the necessary inter-particle correlations, at least five orientationally-dependent virials must be calculated.

We have also examined the effects of confining the columnar phase of these particles. In circumstances where an integer number of columns do not fit neatly into the confining box or cylinder, our simulations indicates the columns either spiral (see the figure) or, more dramatically, break up to form a cubatic-like structure that more effectively fills space.

![Saturn-ring particles consist of a concentric sphere and thin disc. Depending on the relative sizes of the disc and sphere, simulation reveals a variety of unusual crystalline phases and, for the large discs, a nematic phase. A high level virial approach was found to predict the isotropic and nematic properties of this system to high accuracy.](image)

Fig. 1.

Saturn-ring particles consist of a concentric sphere and thin disc. Depending on the relative sizes of the disc and sphere, simulation reveals a variety of unusual crystalline phases and, for the large discs, a nematic phase. A high level virial approach was found to predict the isotropic and nematic properties of this system to high accuracy.

References:
MELTING/FREEZING PHASE TRANSITIONS IN CONFINED SYSTEMS

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The numeric experimental data already collected in the literature indicate the strong influence of the system confinement on the temperature and the peculiarities of phase transitions. This is of a special importance for the melting, freezing, glass-transition, etc. in nanosize objects.

In this contribution we propose the unified thermodynamic approach to the analysis of melting/freezing phenomena in confined systems. The approach is based on the Clausius-Clapeyron relations for coexistence of solid and liquid phases jointly with equations relating the vapour pressures above bulk (with plane interfaces) and confined states of substance. For the illustration we have applied our analysis to three types of confinement: plane interfaces, small particles and pores. It is important to note that the above approach allows to predict the shift of triple point not only for the substance in the core of a pore or of a small particle, but also for the boundary layers of curved system, that is to predict the premelting/prefreezing in skin layer. Although the equations derived allow to calculate the magnitudes and the signs of the shift of the triple point temperature, their main advantage consists not in the predictive power but in the ability to solve the inverse problem. Namely, on the basis of reliably measured shifts of melting/freezing temperatures one can extract the basic information about the structure and properties of boundary phases, surface energies as well as their temperature dependences.
CONDENSATION AND NUCLEATION IN A WEDGE-PORE

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We have considered the equilibrium between vapour, liquid and solid in a wedge-pore on the basis of previous and new work on capillary condensation with a surface force apparatus. Substances allowed to capillary condense from vapour in an annular wedge-pore of mica remain liquid at substantial temperature depressions $\Delta T$ below the bulk melting point $T_m$ [1]. This is an example of thermodynamic or equilibrium supercooling of a liquid, like melting-point depression in porous media. In the wedge-pore, however, the supercooled liquid is in equilibrium with vapour and the amount of liquid (proportional to the radius of curvature $r$ of the liquid-vapour interface) depends on the surface tension $\gamma_{LV}$ of the liquid, not the interfacial tension between solid and liquid $\gamma_{SL}$ [2]. For a near-wetting liquid at coexistence the wedge will fill to a wall separation (opening) $d$ of

$$d = \frac{2V_m \gamma_{LV} T_m}{\Delta H_{fus} \Delta T} \tag{1}$$

where $V_m$ is the molar volume and $\Delta H_{fus}$ the enthalpy of fusion. However, the Gibbs-Thomson equation applied to a wedge-pore predicts that nucleation of solid (freezing of the liquid) should occur for

$$d > \frac{6V_m \gamma_{SL} T_m}{\Delta H_{fus} \Delta T} \tag{2}$$

So, if $3\gamma_{SL} < \gamma_{LV}$ the outer part of the condensed liquid should freeze. For a given $d$ the freezing $\Delta T$ is $3/2$ times the melting $\Delta T$, so in between these two temperatures the liquid will be genuinely (kinetically) supercooled.

We have experimentally verified Eq. (1) for the condensation of water and cyclohexane [3], including its extension to vapour pressures off solid-vapour coexistence. For water, with $\gamma_{LV} = 76$ mJm$^{-2}$ and $\gamma_{SL} \approx 29-34$ mJm$^{-2}$ at 0°C [4], the observed absence of freezing is expected, but with cyclohexane ($\gamma_{LV} = 27$ mJm$^{-2}$ and $\gamma_{SL} \approx 5-6$ mJm$^{-2}$ at $T_m = 6.6$°C) the lack of freezing down to $\Delta T = 14$K must be due to genuine supercooling beyond that predicted by equation 2. In the case of most other studied liquids the uncertainty in the value of $\gamma_{SL}$ makes it difficult to establish the real magnitude of supercooling.

The application of Eq. (1-2) may rationalise earlier results on the growth of solid deposits of neo-pentanol and tetrabromomethane from slightly undersaturated vapour in mica wedges [5]. Heterogeneous nucleation of solid (or liquid) from vapour usually requires substantial supersaturation of the vapour phase, but it is possible that capillary condensation of liquid in surface cracks followed by nucleation of solid in the liquid condensate may be a route to nucleation of solid from vapour close to saturation.

References:
STRUCTURE AND DYNAMICS OF MONOLAYER FILMS FORMED ON CRYSTALLINE SURFACES OF SQUARE SYMMETRY

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It is demonstrated that monolayer films formed on a crystal surface of square symmetry can order into different structures depending on the properties of the surface potential and the misfit between adatoms and the surface lattice. When the surface potential is strongly corrugated the film orders into commensurate structures. On the other hand, when the surface potential is only weakly corrugated the film form incommensurate structure of triangular symmetry. The results of recent Monte Carlo simulation have demonstrated [1], however, that monolayer films formed on a square lattice of sites can order into a novel phase in which every adatom has 5 nearest neighbors. This structure is known as the Archimedean tiling (AT) of type \((3^2.4.3.4)\) [2]. This type of tiling has been found in layered crystalline structure of complex metallic alloys (known as Frank-Kasper phases), supramolecular micellar complex phases of organic dendrons as well as in two-dimensional three-component copolymer mixtures. The formation of such complex phases has never been observed experimentally as well as in experiment as well as in computer simulation studies of simple monolayer films formed by atomic adsorbates.

The main objective of this contribution is to present the mechanism leading to the formation of AT phase and to elucidate the effects of the periodic surface potential and the misfit between adatoms and the surface lattice on the stability of AT.

It is demonstrated that AT develops via small displacements of adatoms from the registry positions. Ground state calculations as well as Monte Carlo simulation demonstrate that the stability of the AT phase depends on the misfit between the adsorbate and the surface lattice as well as on the properties of the surface corrugation potential. The AT phase may be stable at the ground state or develop at finite temperatures from the commensurate c(2x2) structure, via a sharp first-order phase transition. The AT phase remains stable over a certain temperature range, and then it undergoes a transition to either the partially ordered phase of square symmetry or to the incommensurate floating phase of triangular symmetry. In both cases a further increase of temperature leads to the formation of a liquid-like phase via continuous Ising-like phase transition.

Also, the dynamics of monolayer films formed by atomic adsorbates on a square lattice is discussed. The vibrations of films ordered into the commensurate c(2x2) phase, into the incommensurate phase of triangular symmetry as well as into the AT phase are considered. The dispersion relations and densities of states are determined and discussed in the framework of harmonic approximation.

References:
ELECTRIC INTERACTIONS IN ADSORPTION MONOLAYERS: PAIR INTERACTION POTENTIAL, SECOND VIRIAL COEFFICIENT AND INTERACTIONS IN CHARGED HETEROGENEOUS MONOLAYER

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A pair interaction potential for molecules in a monolayer is proposed, which takes into account the dipole-dipole interactions of the normal [1] and tangential component of the surface dipoles, the London dispersion forces and the steric repulsion between adsorbed molecules. Based on these data, the van der Waals attraction constant in the equation of state of the monolayer [2] can be estimated.

The molecular characteristics constituting the potential can be obtained experimentally or from molecular simulations [3]. Atomistic simulations provide normal and tangential monolayer dipole moments of non-ionizable surfactants at different areas per molecule. The van der Waals part of the potential energy is compared to the behaviour predicted by the equation of state. The angular distributions of the tangential dipole moment in the monolayer plane yielded by the two approaches are compared.

The interactions in a heterogeneous monolayer consisting of two surface phases of different degree of dissociation are discussed. Attention is paid to nuclei formation at phase transition in monolayers and to the stability of thin two-dimensional films. A two-dimensional analogue of the disjoining pressure is proposed and calculated [4].

References:
CURRENT PROBLEMS IN KINETICS OF WETTING AND SPREADING

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Based on the isotherm of disjoining pressure the spreading law was predicted in the case of complete wetting and the comparison with experimental data showed an excellent agreement [1,2]. The spreading of surfactant solutions over hydrophobic surfaces was considered from both theoretical and experimental points of view [3,4]. It is shown that the transfer of surfactant molecules from the water droplet onto the hydrophobic surface changes the wetting characteristics in front of the drop on the three-phase contact line. The spreading of small liquid drops over porous layers (dry or saturated with the same liquid) has been investigated in the case of both complete wetting (silicone oils of different viscosities) and partial wetting (aqueous SDS solutions of different concentrations) [7,8]. Theory predicts that (a) the dynamic contact angle dependence on the dimensionless time should be a universal function, (b) the dynamic contact angle should change rapidly over an initial short stage of spreading and should remain a constant value over the duration of the rest of the spreading process. These predictions are in the good agreement with our experimental observations. A moving circular wave front forms after a small droplet of aqueous surfactant solution is deposited on a thin aqueous layer. The time evolution of the radius of the moving front was monitored [5]. Surfactants of different solubility were used at concentrations above cmc. It is shown that the time evolution of the moving front proceeds in two stages: a rapid first stage, which is followed by a slower second stage. It is shown that the time evolution of the moving front substantially depends on the surfactant solubility. Experiments on spreading and evaporation of sessile droplets on a solid substrate under various conditions were reported and compared to the developed theoretical model [6].

References:
EQUILIBRIUM INTERACTIONS BETWEEN CHARGED SURFACES IMMERSER IN A POLYELECTROLYTE SOLUTION

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Using two fundamentally different simulation techniques, we have calculated interactions between like-charged surfaces immersed in a polyelectrolyte solution. In contrast to previous simulations of such systems, we have imposed full equilibrium conditions, i.e. we have included diffusive equilibrium with a bulk solution. This has a profound impact on the resulting interactions: even at modest surface charge densities, oppositely charged chains will adsorb strongly enough to over-compensate the nominal surface charge. This leads to a repulsive barrier, where the long-ranged tail is dominated by double layer interactions. Previously studied canonical approaches, where the chains are assumed to perfectly neutralize the surfaces, will not capture this stabilising barrier. The barrier height increases with the length of the polions. Interestingly enough, the separation at which the repulsion turns attractive, is independent of chain length. The shortest chains are here unable to stretch across from one surface to the other. Hence, it is not bridging, at least not in this traditional sense, that initiates the attraction (although bridging does dominate at short separations). We find that polyion-polyion correlations play a crucial role at the free energy barrier. We have also investigated responses to salt addition, and changes to the polyelectrolyte concentration. The simulation data are in qualitative and semi-quantitative agreement with experimental findings. Our work furthermore include comparisons with density functional predictions, establishing that the stabilising barrier depend strongly on ion-ion correlations. Hence, we here observe repulsion, due to ion-ion correlations, between like-charged surfaces at long range. Finally, we have evaluated the performance of two different simulation approaches. Invoking configurationally weighted schemes, it is possible to run grand canonical simulations on these systems. However, when the chain length exceeds about 15 monomers, this method becomes very computationally demanding. In order to handle such systems, we have developed a simulation technique that makes use of the isotension ensemble. For long chains, this approach completely outperforms the grand canonical scheme.
THE INTERACTION BETWEEN CHARGED SURFACES INDUCED BY NANO-PARTICLES

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The mean field theory could not be used to describe highly charged systems. More advanced methods have to be used in order to introduce the correlations between highly charged particles. Here we focus on the system of highly charged surfaces [1], separated by a solution of nano-particles with spatially distributed charges [2]. Our nano-particles possess dipolar or quadrupolar moments. The system is theoretically described by using functional density theory [3,4]. The minimization of the system is performed to obtain the equilibrium configuration of the system. The solution of the variational problem shows that orientational ordering of nano-particles in the field of the system give rise to attractive interaction between equally charged surfaces [4]. Further it was shown that for large enough dimensions of nano-particles and large enough surface charge densities of surfaces, the two equally charged surfaces could experience an attractive force due to the spatially distributed charges within the nano-particles.

References:

HYDRODYNAMIC CRYSTALS: COLLECTIVE DYNAMICS OF REGULAR ARRAYS OF SPHERICAL PARTICLES IN A PARALLEL WALL CHANNEL

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Simulations of over $10^3$ particles are used to investigate collective motion of linear trains and regular square arrays of spherical particles suspended in a fluid bounded by two parallel walls driven by the parabolic flow, see figure. Simplifications associated with the Hele-Shaw asymptotic far-field form of the flow scattered by the particles are the basis of our novel accelerated Stokesian-dynamics algorithm. The results demonstrate propagation of particle-displacement waves, deformation and rearrangements of a particle lattice, evolution of dislocation defects in ordered arrays, and prolonged coexistence of ordered and disordered regions. In confined multiphase systems, the collective particle behavior is strongly influenced by the bounding walls. Hydrodynamic confinement effects are especially significant in parallel-wall channels of the width comparable to the particle size. Lateral motion of individual particles in such a channel produces fluid backflow (unlike the corresponding behavior in free space). The backflow enhances relative particle motion [1-3], considerably increases transverse hydrodynamic resistance for elongated rigid arrays of spheres moving parallel to the channel walls [2-4], and governs propagation of particle-displacement waves [5,6] in linear arrays of drops in a microfluidic channel. We show that the fluid backflow resulting from the motion of an individual particle is also responsible for pattern-formation phenomena occurring in 2D hydrodynamic crystals, i.e. regular particle arrays that are hydrodynamically driven.

Our system has a number of interesting features. First, the pattern formation occurs in the linear Stokes-flow regime - the nonlinearity stems entirely from the position-dependence of the multiparticle mobility matrix. Next, the dipolar hydrodynamic interactions that maintain particle ordering are non-isotropic (causing, e.g., lattice reorientation). Finally, the dipolar flow that maintains the ordered lattice structure on the local level also produces the macroscopic deformation of the array, leading to lattice instabilities. Since regular particle arrays can be assembled using holographic optical tweezers the complex collective dynamic phenomena revealed by our study should be accessible experimentally.

References:

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Fig. 1.}
\end{figure}
OPTICAL TRAPPING STUDIES OF COLLOIDAL INTERACTIONS IN LIQUID FILMS

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Optical trapping of colloids in liquid films provides a unique tool to investigate the long range interactions characterizing systems of reduced dimensionality. Optical tweezers allow the positioning of two beads at varying separations, isolated from boundaries and other particles. Controlled force fields can be then applied and used to gauge interparticle forces.

We measure hydrodynamic interactions between colloidal particles confined in a two dimensional fluid. The reduced dimensionality compared to a bulk fluid increases dramatically the range of couplings. Using optical tweezers we can force a two body system along the eigenmodes of the mobility tensor and measure the corresponding eigen-mobilities which change logarithmically with particle separation [1]. We derive the two dimensional counterpart of the Oseen hydrodynamic tensor, which quantitatively accounts for the experimental observations. These results highlight the importance of dimensionality in colloidal systems, for example in the understanding of diffusion and interactions of proteins in biological membranes.

Micron-sized objects confined in thin liquid films interact through forces mediated by the deformed liquid-air interface. These capillary interactions provide a powerful driving mechanism for the selfassembly of ordered structures such as photonic materials or protein crystals. We demonstrate how optical micro-manipulation allows the direct measurement of capillary interactions between mesoscopic objects [2]. The force falls off as an inverse power law in particles separation. We derive and validate an explicit expression for this exponent whose magnitude is mainly governed by particle size. For micron-sized objects we found an exponent close to, but smaller than one, making capillary interactions a unique example of strong and very long ranged forces in the mesoscopic world.

References:
HOW DOES A PATTERNED SUBSTRATE INFLUENCE THE IRREVERSIBLE ADSORPTION OF COLLOIDAL PARTICLES?

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Irreversible adsorption of colloidal particles at surfaces poses interesting challenges, from a theoretical and experimental point of view. To control adsorption of colloids at surfaces, it is common practice to resort to patterns. We present simulational studies of the irreversible adsorption of particles on patterned substrates, which allows control of film morphology and, consequently, of its physical properties. For the sake of simplicity, the pattern consists of squares embedded on a square lattice matrix, such that adsorption only takes place inside the squares. We study the influence of the pattern on both jammed state morphology and adsorption kinetics is studied by extensive Monte Carlo simulations.

A model including only excluded volume interaction between particles, which has been studied extensively by Monte Carlo simulations [1,2], can be parametrized in terms of $\alpha$ and $\beta$, the size of squares and their separation in units of particle diameter, respectively. The model represents a generalization of the Random Sequential Adsorption one with a rich set of 'phases' present. Such 'phases' appear due to the interplay between the maximum number of particles adsorbed per cell (single-particle or multiparticle) and by the level of interaction between colloids adsorbed in neighboring cells (non-interacting or interacting).

Finally, we also report the influence of the pattern on the kinetics of adsorption. Proper tuning up of the $\alpha$ and $\beta$ parameters can lead to either a power-law or exponential approaches to the jamming coverage. Measurements of the distribution of areas available for adsorption during the process make possible to predict how the jammed state is attained.

One of the goals of the present study regards the relevance of geometrical restrictions on the irreversible formation of single-layer colloidal films with potential for practical applications.

References:
MODELING OF ATTRACTIVE AND REPULSIVE ELECTROSTATIC INTERACTION IN THE PROCESS OF MULTILAYER RANDOM SEQUENTIAL ADSORPTION

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Monte Carlo random sequential adsorption (RSA) modeling is a simple and effective method for computer simulation of localized, irreversible adsorption phenomena. Although the classical model deals with the simplest problem of hard, monodisperse spheres at a homogeneous interface, the approach can be extended to include a number of effects, e.g., particle anisotropy or polydispersity, Brownian motion, external force, electrostatic interaction or surface heterogeneity. The approach, being an alternative for the Brownian dynamics simulation, is computationally much cheaper and effective. In this presentation we discuss the extension of the approach allowing simulation of multilayer adsorption of electrostatically charged, monodisperse spheres. We use the model to describe the process of multilayer thin film formation as it occurs in experimental systems applying the method “layer by layer”. The method allows prediction of the multilayer structure in terms of 2D and 3D pair-correlation function, as well as the multilayer density distribution. We present the results of simulations of a multilayer composed of twenty monolayers, obtained for several values of first layer surface coverage and electrolyte ionic strength. Our results suggest that the porosity of multilayers formed at lower ionic strength is higher. We also demonstrate that with the increase of first layer surface coverage the local ordering of adsorbed multilayer changes from spherical to planar.
SYNERGETIC PRINCIPLE OF PROTEIN FUNCTIONING

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The ability of proteins to co-ordinate fast reaction events in their active centers with slow re-arrangements of their structure is focused upon. Under real conditions of many sequential reaction turnovers of the biomacromolecule the structural shifts caused by single turnovers can be of cumulative character. This, in turn, leads to drastic threshold-like changes of the reaction cycle. In that way the creative role of dynamical substrate-conformation interactions in forming of the functional regimes of the protein-enzyme is consistently uncovered for the first time. With this, isolated data on the complex behaviour of macromolecules (non-exponential relaxation, memory of reaction cycles, folding peculiarities, non-Michaelis kinetics and non-Langmuir saturation, cooperativity of non-oligomeric or non-allosteric enzymes, etc) turn out to be a manifestation of the unified effect of dynamical intramolecular self-organization as one of the basic principles of molecular machines at work.

The consideration is based on the development of modern stochastic theory of non-equilibrium phase transitions, extended to the level of single molecules [1,2], and comprises analytical and computer modeling of the generic reaction schemes of charge transfer and ligand binding, design and simulation of decisive experiments as well as the proofs of realization of the mentioned mechanisms and effects in specific biomolecular processes (photosynthetic charge separation, reactions of single enzymes and others [3,4]).

References:
MONTE CARLO SIMULATION STUDIES OF MICROEMULSION-ABA-TRIBLOCK COPOLYMER SYSTEMS

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The structural and dynamic properties of a system composed by water-in-oil microemulsions changes significantly by the addition of hydrophobically end-capped polymers. The favourable interaction between the hydrophobic ends and the oil interior of the droplets leads to restrictions of the conformational behaviour of the polymers. The chains tend to adopt either loop conformations, where both ends are located inside the same droplet, or to bridge conformations, where each end is located in different droplet. Although both situations influence the droplet distribution and the dynamic behaviour of the system, extensive bridging results in a phase transition from a sol to a physical gel.

Monte Carlo simulation was used to study how polymer and droplet properties are influenced the structure of polymer-microemulsion networks. In our model each chain was considered as a sequence of point particles connected by harmonic bond potentials and the intrinsic stiffness of the chain was regulated through an angular potential. The distinction between hydrophobic and hydrophilic segments was made by imposing a different interaction with the interior of the droplets. The structural aspects of the system were studied using polymer end-to-end probability distributions, droplet-droplet nearest-neighbour distributions, and several different connectivity indicators.

The results showed that the distribution of droplets is significantly influenced by the chain properties. The fraction of polymers forming bridges was found to correlate well with the ratio between the end-to-end separation of unperturbed polymers and the surface-to-surface separation of neighbouring droplets at a lattice arrangement, independently of the polymer of droplet characteristics, but the fraction was found to be independent of the number ratio of polymers and droplets. Chain stiffness was established as an important variable for controlling the efficiency of bridge formation. Long polymers induced depletion attraction among droplets.

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MONO AND DIACYL LYSINE BASED SURFACTANTS: SELF-AGGREGATION

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Self-aggregation and surface properties of several acyl and diacyl lysine based surfactants have been studied. These surfactants are biodegradable, biocompatible and present some antimicrobial activity. Single chain surfactants with varying hydrophobic chain length were studied; their structure is presented in Fig. 1. The cmc values are close to the expected for ionic surfactants with the same chain length. The aggregates were studied by NMR diffusometry the results suggest notable anisometry as the chain length is increased. At higher concentration gel and liquid crystalline phases have been identified by optical microscopy and SAXS. Lamellar and cubic phases are present at high concentration.

Diacyl lysine surfactants, shown in Fig 2, are highly biodegradable, with low toxicity, ecotoxicity and irritation effects. For this reason, they are potential candidates for pharmaceutical and cosmetic applications. We have studied the aqueous solution aggregation properties for several surfactant counterions at a fixed hydrophobic chain length. They present a low cmc nearly independent of counterion. The area per surfactant molecule is around 1.3 nm$^2$ also independent of counterion. We have also studied the dry state crystallisation of these surfactant salts, the increase in counterion size tends to form lamellar structures. We have compared this behaviour with the dry state crystallisation of the acidic compounds as a function of hydrophobic chain length.

![Fig. 1. N$^\varepsilon$-Lysine methyl ester surfactants](image1)

![Fig. 2. N$^\alpha$, N$^\varepsilon$-Diacyl Lysine surfactants](image2)
SYNTHESIS AND OPTICAL CHARACTERIZATION OF SURFACE-FUNCTIONALIZED INORGANIC-ORGANIC MULTILAYER PARTICLES

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We report on the preparation of a variety of surface-modifiable inorganic particles with controlled morphology, size and shape, achieved by tuning different physical and chemical parameters (nature of precursor, concentration, pH, temperature, solvent...). We focus on the synthesis of colloidal ZnO and α-Fe$_2$O$_3$ (hematite) particles exhibiting interesting optical (high refractive index, anisotropy) and/or magnetic properties [1,2].

These particles can then be coated with a silica layer of a controlled thickness [3,4], allowing the further creation of a specific surface functionality for their incorporation in polymer matrices or simply for their stabilization in a desired solvent. We also show that an additional coating step with an organic layer using dispersion polymerization or controlled growth from the surface of the silica shell is possible, leading to core-shell-shell particles with interesting tuneable surface properties. We finally present results on the optical properties of those systems and their promising applications as microrheological tools and in colloidal crystals and glasses.

Fig. 1. ZnO-SiO$_2$ and α-Fe$_2$O$_3$-SiO$_2$ core-shell particles.

References:
OXIDATION OF Fe(OH)$_2$ IN THE PRESENCE OF KNO$_3$: A VERSATILE METHOD FOR THE FABRICATION OF MAGNETIC COLLOIDAL PARTICLES

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The precipitation of Fe(OH)$_2$ and its subsequent oxidation in aqueous media in the presence of KNO$_3$ has been known for decades as a relatively simple method for the fabrication of magnetite particles [1]. In order to prepare novel magnetic particles and fluids, our group has revisited this process, which has proved to be very versatile. Small modifications in the ionic composition of the reactant mixture can result in magnetite particles of very different typical size (from 50 nm to 600 nm), or in the incorporation of other divalent metallic cations, such as Ni$^{2+}$ or Co$^{2+}$, to form non-stoichiometric spinel ferrites. Furthermore, if the particle growth takes place at a pH close to that of magnetite, which occurs when there is an excess of Fe$^{2+}$ in the supernatant, the growing particles can be self-assembled into permanent micron-sized linear aggregates by the superposition of a uniaxial external magnetic field. We will present a detailed description of this synthesis method, as well as of the properties of the particles that we have fabricated to date. These include (Figure 1): i) micro rods of magnetite [2], ii) micro rods of Ni and Co ferrites [3], iii) single-domain monocrystalline magnetite [4], and iv) hollow spheres and micron-sized rods of Ni-ferrite.

Fig. 1. Scanning electron micrographs of, magnetite microfibers (A) monocrystalline magnetite nanoparticles (B) and hollow Ni-ferrite microfibers (C).

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References:
POLYMER-GRAFTED SİLİCA NANOPARTİCLES: FROM COLLOİDAL SOLUTİON SYNTHESIS TO THE DISPERSION IN A COMPOSITE MATRİX FİLM

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We are interested in nanocomposites formed by inclusion of silica nanoparticles in a polymer matrix. We aim at controlling the dispersion state so as to control the macroscopic properties of the composite. We use the synthesis technique named „grafting from“ [1] which consists in starting a polymerization from the particle surface (by Nitroxide-Mediated Polymerization, NMP).

We established a reproducible grafting protocol of polystyrene on Ludox silica nanoparticles. Initially dispersed in water, they are transferred into an organic solvent without disturbing colloidal stability; and during the whole process of polymerization in solution, the stability is kept. Small-Angle Neutron Scattering (SANS) measurements allow characterizing the final objects: we can observe separately the signal of the particles and the signal of the shell of polymer using the contrast variation method: matching the corona gives the structure factor between the centres of the grafted objects, whereas matching the core gives the form factor of the grafted polymer part. Fitting the scattering curves yields then the parameters of the grafted particles form factor, which agree very well with chemical analyses. One can observe that different models can be used depending on the sample: in some case the Pedersen model permits to describe a corona of individual chains immersed in the solvent, in another the best model is a core-shell one, with a corona with sharp interface with solvent.

After characterization in solution, the grafted particles are mixed with polymer chains in presence of solvent which is then evaporated to form composites. If neither the grafted polymer nor the matrix are deuterated, with SANS we “see” only the silica particles and their dispersion. To see only the grafted deuterated corona signal, we have synthesized a special matrix: a copolymer of deuterated and non deuterated styrene in such proportions that it matches the silica scattering. We can thus follow both the silica and the corona scattering inside the matrix, from the isotropic state (at rest) to the anisotropic one for stretched samples (see sketch).

References:
A SIMPLE “GREEN” CHEMISTRY ROUTE FOR NANOSTRUCTURED METAL NITRIDES SYNTHESIS

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Metal nitrides are intriguing materials able to be applied in many different fields (such as biomedicine, catalysis, electronics and semiconductor industry) thank their peculiarities. They can show optical, electronic and magnetic properties and possess high strength and durability; as a consequence, they are very versatile materials of high technological interest. Furthermore, metal nitrides potentialities can be enhanced by finely dispersing them in form of small nanoparticles.

A simple, inexpensive and “green” route for the synthesis of nanostructured metal nitrides (such as Mo$_3$N$_2$, WN, VN, TiN, etc) has been set up lately. Starting from an appropriate metal precursor solution has been possible to prepare metal nitride of different metals using urea to play the double role of nitrogen source and stabilizing agent (necessary for the nanoparticle dispersion). Metal nitrides synthesized are almost pure and highly crystalline, with sizes ranging between 5 and 40 nm in diameter (depending on the metal nitride). Their use is exemplified in model reaction: thus a high catalytic activity for the C-C coupling of alcohols and ketones reaction is observed.

Fig. 1. WAXS diffraction pattern and corresponding TEM micrograph of TiN nanoparticles.
FOOD GRADE MICROCAPSULES: FROM SIMPLE MATERIALS TO SMART DELIVERY VEHICLES

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Targeted and controlled delivery of drugs or probiotics is a major goal for the pharmaceutical and food industry. For efficient smart delivery, microcapsules should have sufficient (mechanical) stability, a well defined permeability to the encapsulated material, present a release trigger mechanism, and ideally be monodisperse. Also, especially for food applications, its shell has to be food-grade and inexpensive.

We investigated the production of microcapsules using layer-by-layer adsorption of oppositely charged polysaccharides, proteins, and proteins fibrils (Fig. 1a) or colloidal particles (Fig. 1b) under acidic conditions. While the size of the microcapsule is determined by the template droplet (which is tuned by membrane emulsification), its mechanical strength, and possibly its permeability, is controlled by the number and composition of the adsorbed layers. During the presentation, we will present details on the production and characterization of these novel microcapsules in relation to the various building blocks that were used.

Fig. 1: SEM pictures of the microcapsules obtained by the electrostatic layer-by-layer adsorption. a) protein/pectin/protein fibril system, b) protein/pectin/colloidal particle system

References:
NANOPARTICLES PRODUCTION USING LIQUID-LIQUID INTERFACIAL REACTOR

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In recent years interest in nanotechnology has increased significantly in the manufacture and functionalisation of nanoparticles, increasing the demand for nanoparticles as building blocks. The aim of this project is to develop a fully scalable interfacial reactor for nanoparticle production. These materials have potential applications in various industries such as electronics, fine chemicals, catalysis, cosmetics, pharmaceutical, healthcare and medicine.

Noble metal nanoparticles can be readily grown at the interface of two immiscible liquids, where one of the liquids carries the precursor cation for the material while the other one carries the reducing agent. Reduction of the cation at the interface leads to formation of nanoparticles [1]. Flow rate of the two immiscible liquids will be utilised to control morphology of the particles.

The idea of synthesising nanoparticles at liquid-liquid interface and using flow to control their growth and separation is novel and relevant as particles assembled at such interfaces often show size segregation and defect ‘healing’ phenomenon [2]. This way of nanoparticle production also has the benefit of being a continuous process and is a fully scalable route to manufacturing these kinds of materials.

References:
GROWTH OF TiO$_2$ NANOPARTICLES BY PULSED LASER ABLATION (PLA) IN LIQUID MEDIA AND STUDY OF PHOTOCATALYTIC PROPERTIES

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Oxide semiconductors, such as TiO$_2$ nanocrystals, have extensively been studied for their high photocatalytic, hydrophilic, chemical stability properties and for a variety of applications. We do not have pure nanoparticles in chemical methods because of having byproducts. Furthermore, in chemical methods nanoparticles are amorphous, so for increasing the crystallinity we have to anneal TiO$_2$ nanoparticles for postcalcination, so inevitably resulted in the size increase and agglomeration of TiO$_2$ nanoparticles, so for synthesis of nanoparticles we have used laser ablation physical method in liquid phase and we have studied the photocatalytic properties, crystallinity and size distribution. Some of the advantages of this method are: purity of nanoparticles, being a simple method, being inexpensive, controllable size and possibility for growth of nanoparticles in desired liquid environment.

We synthesized ultrafine TiO$_2$ nanoparticles by pulsed laser ablation of a Titanium target immersed in an aqueous solution of surfactants such as Sodium Dodecyl Sulfate (SDS), Carboxy Methyl Cellulose (CMC) and also in different liquid medias, such as deionized water, Acetone, Ethanol, 2-Propanol and Acetyl Acetone. The surfactant concentration dependence of TiO$_2$ nanocrystal formation was systematically investigated by various characterization techniques. In different aqueous solution of SDS, the maximum amount of ultrafine anatase nanocrystalline particles was obtained in an aqueous solution of 0.001 M SDS. Single-phase anatase nanoparticles with a mean size of 8 nm were obtained in a 0.001 M SDS solution. In different aqueous solution of Acetyl Acetone, the maximum amount of ultrafine anatase nanocrystalline particles was obtained in an aqueous solution of 0.001 M Acetyl Acetone and the sizes are below 10nm. As TiO$_2$ is a famous photocatalyst, we have also done photocatalytic test by Methyl Orange under UV irradiation for prepared samples. We have studied the effect of liquid media, surfactant concentration and laser energy on size and optical properties of nanoparticles. The experiments was done by a pulsed Nd:YAG laser. We used UV/Vis Spectroscopy, XPS, XRD, SEM, TEM and DLS for characterization.

Fig. 1. TEM image and size distribution for a typical sample that is ablated in 2-Propanol. The average dimension is 9.2 nm.

References:
COLLOIDAL TECHNIQUE FOR ZnO/MgO NANOCATALYSTS PREPARATION

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Materials made of small particles of zinc oxide are widely used in diverse areas such as solar cells, luminescent devices, gas sensors, catalysts, etc. The possible application of ZnO nanoparticles is based on use of their unique physical and chemical properties which differ essentially from those of bulk materials and which strongly depend on particles size, size distribution, and morphology. ZnO nanoparticles may be perspective for application in catalysis as support, active component, promoter or as structural and textural modifier of catalysts. Various methods of chemical synthesis have been employed to prepare the ZnO nanostructures such as self-assembly, template assisted sol-gel, laser vaporization/condensation, thermal decomposition, flame spray pyrolysis, mechanochemical process, etc. However, most of these processes induce irregular particle shape and wide size distribution.

The method based on preformation of colloidal particles, which subsequently are deposited on a support, may be used for preparation of supported nanomaterials. This colloidal method gives a possibility to obtain the highly uniform nanoparticles and to control the morphology of the prepared solids.

We have proposed a relatively simple method for preparation of magnesia supported ZnO nanoparticles with controllable size. The developed approach is based on deposition of zinc oxide nanoparticles from colloidal solution without surfactant on magnesia. The ZnO nanoparticles colloid was obtained by mixing of 2-propanol solutions of zinc acetate and sodium hydroxide followed the method of Bahnemann et al. [1,2] with some modifications. The synthesis of ZnO/MgO solid was carried out by mixing of ZnO colloidal solution with magnesia suspension in 2-propanol followed by filtration, washing, drying and calcination. The size of ZnO nanoparticles in obtained ZnO/MgO solids is controlled by conditions of their growth in colloidal solution: concentration of initial reagents, pH value, temperature and time of aging. The solids obtained by this route contain ZnO nanoparticles with different size (3-7 nm in diameter) and have constant composition (ca. 1 wt. % ZnO). The morphology of the ZnO nanoparticles was investigated by transmission electron microscopy and UV-Vis absorption and diffuse reflectance spectroscopy. The combined use of both these methods ensured a trustworthy information about the morphology and size of ZnO nanoparticles in colloid as well as in solid.

The catalytic properties of prepared ZnO/MgO solids with variable size of supported ZnO nanoparticles were tested in the CO oxidation reaction by a flow method. The nonmonotonic dependence of catalytic activity on ZnO nanoparticles size was found. The ZnO/MgO solid containing ZnO particles with average size about 4.4 nm has maximum activity in CO oxidation reaction.

**References:**


DESIGN OF SURFACTANTS AND PROPERTIES OF COLLOIDAL
NANOPARTICLES USED IN LUBRICANT ADDITIVE
FORMULATIONS

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Additives are used in lubricants to minimise destructive processes in the engine (e.g. wear and corrosion) and to confer beneficial properties (e.g. improved fuel economy). Overbased detergents are an integral element of such systems, and consist of surfactant stabilised inorganic nanoparticles (comprising calcium carbonate). Such “overbased” additives represent “model” hard-sphere systems with narrow polydispersity and mean core radius ~2 – 5 nm. They have been characterised by a range of techniques including small-angle neutron scattering (SANS). Overbased detergents are used in lubrication packages to provide protection against corrosion and provide detergency in the engine, in particular piston cleanliness and prevention of sludge formation.

This talk will focus on the design of surfactants for stabilising nanoparticles using studies of mixed surfactant systems (comprising a homologous series of di-alkyl anionic surfactants based on Aerosol-OT analogues with linear and branched alkyl chains). The use of such mixtures can provide synergistic enhancement of properties. Air-water interfacial measurements and studies of water-in-oil microemulsion suggest that mixtures of linear and branched analogues give rise to surprising and unexpected behavior: apparently a strong interfacial partitioning of branched chain surfactant at the expense of the linear chain relative (non-idealities). This behavior is not predicted by the established theories (of ideal mixing).

In addition, studies of properties involving detergent nanoparticles will be presented; in particular their interaction with other species found in the engine. Results will be contrasted with data obtained from engine testing. Specifically the following interactions will be discussed:

Acid Neutralisation: Detergents neutralise acid species introduced into the lubricant through acidic blow-by gases. With the increased use of exhaust gas recirculation in diesel engines (used to reduce the level of NO\textsubscript{x} by reducing combustion temperature), there is increased interest in the factors affecting acid neutralisation kinetics.

Water: Water is a by-product of both combustion and acid neutralisation and can enter the lubricant. This can be dispersed in the form of emulsion droplets (stabilised mechanically or with amphiphilic additives present in the lubricant). Recent (SANS) studies have shown that water can form monolayers on the surface of the detergent, which influence the colloidal properties of the system.
SELF-ASSEMBLED ELECTRODES FOR FUEL CELLS

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To combat problems with performance consistency and manufacturing costs of Proton Exchange Membrane Fuel Cells (PEMFC, see figure) a new design has been envisaged that is built entirely out of spontaneously self-assembling components leading to a controlled structure of the cell at the nanoscale, guaranteeing highly tuneable properties and reduced independency on current material suppliers.

Assembly starts by forming a bicontinuous microemulsion of amphiphilic fluorocarbon monomers in which carbon supported platinum nanoparticles are synthesised in-situ. The monomers are later polymerised to form a rigid framework. The choice of platinum is because of its high electrochemical catalytic activity and a carbon support is required to ensure conduction of electrons. The bi-continuous network promotes fast transport of protons through its interconnected water channels and the fluorinated polymer backbone is essential to form a chemically and mechanically robust structure.

Studies with electrodes formed out of self assembled bicontinuous micro emulsions in which supported platinum catalyst nanoparticles are synthesised in situ have shown promising results.
HYBRID POLYMER SOLAR CELLS: HOW COLLOID SCIENCE BRING DEPLOYMENT A STEP CLOSER

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The need to develop and deploy large-scale, cost-effective, renewable energy is becoming increasingly important. Even though silicon solar cells have high power conversion efficiencies (PCE) they are expensive to produce and have long energy payback times. A cost reduction in solar derived electricity of about an order of magnitude is required to enable widespread deployment. This requires an alternative type of solar cell prepared using wet-processing techniques. In recent years hybrid polymer solar cells containing inorganic nanoparticles (e.g., CdSe, ZnO or PbS) blended with semiconducting polymers have been investigated. These solar cells offer great promise because both components can in principle harvest light. The highest PCE values reported for these solar cells to date is [1] 2.8%. PCE values of at least 10% are required in order for commercialisation to be viable. One of the most important problems restricting the PCE for hybrid polymer solar cells is colloidal in nature. The photoactive layers for these solar cells are prepared using a three component blend of inorganic nanoparticles, conjugated polymer and organic solvent [2]. Solvent evaporation during film formation results extensive phase separation. This results in polymer-rich domains between nanoparticle aggregates within the photoactive layer. These regions cause recombination of the photogenerated charge carriers and decrease the PCE. The ideal photoactive layer would consist of strings of touching, naked, nanoparticles with an average inter-string separation of about 10 nm. The polymer and nanoparticle phases would be bicontinuous. Even though there are a number of colloidal factors that favour nanoparticle aggregation and phase separation during film formation there are others that could be used to prevent this. Hybrid solar cell research is attracting very strong academic interest from physicists and chemists; however, it has not yet attracted significant attention from the colloid and interface science community. This presentation aims to show how colloid and interface science could enable major improvements of the PCEs for hybrid polymer solar cells.

References:
SELF-ASSEMBLED MONOLAYER OF ALKANTHIOLATE ON GOLD SURFACE —APPLICATION TO CATALYSIS

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The building-up of an assembly of designed molecules on a well-defined surface would be an interesting approach towards the development of highly efficient catalysts. However, attempts to utilize such defined monolayer for organic synthesis have not been fully established [1]. We report the modification of gold surface with a caged, compact trialkylphosphine (SMAP) [2] bearing an alkanethiolate pendant and its application to a rhodium-catalyzed dehydrogenative alcohol silylation [3].

The surface density of the phosphine-terminated thiolate molecules was found to be 4.2 molecules/nm² by electrochemical desorption method, strongly suggesting the formation of a monolayer with high P-density. Rh-complexed surface ([Au]-SMAP-Rh) showed high catalytic activity and reusability in dehydrogenative silylation of primary alcohol. Compared with the corresponding surface catalyst bearing the conventional Ph₂P-type coordinating group and with homogeneous Rh catalysts, [Au]-SMAP-Rh exhibited robustness and efficient reusability. In addition, [Au]-SMAP-Rh showed extremely high selectivity (>99.5%) toward primary alcohols in the presence of secondary alcohols.

References:
PHOSPHONATE CARBOXYLATE COPOLYMER DISPERSANTS FOR BOEHMITE

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There is a need for robust dispersants in processing operations such as those encountered in the production of titania pigment. Dispersion throughout titania pigment processing is vital to ensure pigment particles remain discrete upon application of inorganic coatings, ensuring the valuable optical properties of titania are retained.

Polyphosphates are commonly used industrially to provide electrostatic stabilisation during the inorganic oxide coatings applications. Polyphosphates however show instability under processing conditions of high temperature and acidic pH, leading to a loss of dispersion stability and higher aggregation levels in the aqueous pigment slurry. Any new dispersant is required to be stable across a broad pH and temperature range to withstand processing conditions. Phosphonates offer greater thermal and pH stability than phosphates due to the presence of the P-C bond. Consequently we have considered phosphonates as a potential oxide dispersant replacement for the polyphosphates currently used.

In this study, the synthesis and interaction of carboxylate-phosphonate copolymers with boehmite particles is reported. Carboxylate-phosphonate copolymers have been synthesised by free radical polymerisation at two varying copolymer ratios. To model the system for the titania pigment particle we used high purity boehmite as previous surface analysis of the uncoated raw pigment has shown that the surface has a boehmite character. The influence of pH, copolymer ratio and concentration on the electrochemical and rheological behaviour of boehmite suspensions is reported. Adsorption isotherms along with rheological and zeta potential studies were undertaken to determine the interaction of the carboxylate-phosphonate copolymers with the boehmite surface. The variations in rheological properties correlate with the change in the boehmite surface properties. The rheological measurements have shown good dispersion properties while the adsorption isotherms indicated a strong interaction with the boehmite surface.
MEASUREMENT OF THE ROTATIONAL DIFFUSION OF METAL COLLOIDS USING DUAL ANGLE DYNAMIC LIGHT SCATTERING

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In this paper we present Dynamic Light Scattering (DLS) measurements of the rotational diffusion of silver nanoprisms. Traditionally it has been necessary to use Depolarised Dynamic Light Scattering to be able to extract the rotational diffusion coefficient from a DLS measurement, due to the small relative magnitude of the relaxation mode corresponding to rotational diffusion compared to the dominant translational diffusion mode [1,2].

The specific refractive index characteristics of metal particles mean that the rotational mode contribution is large enough to be measured alongside the translational diffusion mode. We propose a two angle measurement, to be able to determine whether a particular relaxation mode is rotational or translational. The Autocorrelation Function (ACF) relaxation time corresponding to a rotational mode is independent of the scattering angle, whereas the ACF relaxation time corresponding to translational diffusion is dependent of angle. Thus, we can determine if a mode corresponds to rotational or translational diffusion by measuring the ACF at two angles and comparing the relaxation times.

We present an example of the technique as applied to colloidal suspensions of silver nanoprisms with constant section and different lengths [3]. We show that for each of the samples two relaxation times can be measured, one corresponding to rotational diffusion, and another one to translational diffusion. The data obtained can then be used to obtain a measurement of the anisotropy of the particles.

References:
SARFUS: ACCESS TO THE NANOWORLD SIMPLY WITH A STANDARD OPTICAL MICROSCOPE

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We present a new technique (Sarfus) that increases the sensitivity of light optical microscopy to a point where it becomes possible to directly visualize nanometric films (down to 0.5 nanometer) and isolated nano-objects in real-time.

The technique is based on the use of new nonreflecting surfaces for cross-polarized reflected light microscopy. These surfaces (Surf) generate a contrast enhancement of about 2 orders of magnitude, extending the application fields of optical microscopy toward the nanoworld. Thanks to the absence of scanning, the dynamic studies of nanometric structures (eg. crystallization, wettability, evaporation, spreading) is easily accessible and opens new potentialities in various fields such as, for example, thin layers, surface treatment, self-organized structures, Langmuir-Blodgett films, biochips, lithography and nanopatterning, carbon nanotubes, nanowires. A 3D reconstitution software (Sarfusoft) makes possible to measure optical thickness, roughness of the samples. The technique can be also designed for integration in existing equipment (AFM, RAMAN) for nano-structures pre-localisation. The efficiency of the method is proven experimentally on well-characterized samples.
QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION MONITORING (QCM-D): A POWERFUL TECHNOLOGY FOR STUDYING SURFACE RELATED MOLECULAR REACTIONS AND INTERACTIONS

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The Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) is a still young yet powerful technology for studying formation of thin films such as proteins, polymers and cells on surfaces, in liquid. QCM-D measures in real-time the mass of molecular layers that form on a piezoelectric quartz sensor. Simultaneously structural (viscoelastic) properties of such molecular layers are monitored, which enables distinction between two similar interactions or observation of a phase transition in bound layers. Measurements of both mass and structural properties gives a thorough understanding of binding events such as molecular adsorption and interaction. Moreover, the QCM-D technique makes it possible to extract water content of molecular layers, in contrast to optical mass measurements, and allows several kinds of substrates such as metals, polymers and functionalised coatings for controlled studies of interactions.

This enables the extraction of various informations about e.g. Kinetics, Affinity, Specificity, Structure, Mass, Film thickness

In this presentation QCM-D technology will be introduced and the information content will be demonstrated on different application examples such as Layer-by-layer assembly, protein adsorption with conformational changes and cell adsorption for the development of biomaterial interfaces.
NT-MDT - Integrated solutions for NanoTechnology

Dimitry Kozodaev

NT-MDT has been creating the equipment for nanotechnology researches for more than 17 years, steadily holding the advanced positions regarding the quality standards/hi-tech developments/original technical solutions.

The range of products constantly expands, and is represented today with different equipment lines. These are the accessories for the probe microscopy; SPMs for educational needs (NanoEducator); specialized SPMs (Solver) for scientific and industrial research centers. These are the probe nano-laboratories (NTEGRA) uniting the whole spectrum of modern techniques on the SPM basis; and, at last, the modular nano-factories (Nanofab) uniting the whole arsenal of means and techniques necessary for processing and quality assurance of devices/elements of micro- and nano-electronics.

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THE "BALANCED CATALYTIC SURFACTANT" CONCEPT: APPLICATION TO THE DESIGN OF THREE-PHASE OXIDIZING MICROEMULSIONS

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Development of surfactants exhibiting catalytic properties is an interesting issue since their localisation at the water-oil interface is likely to increase both the water-oil compatibility and the kinetics of the catalytic reaction. A new class of catalytic surfactants, called "catasurfs", based on double-tailed \([\text{C}_n\text{C}_m\text{N}((\text{C}_1)_2)_2]^+ (n, m = 6 - 12)\) ammonium groups electrostatically bound to a catalytic counter-ion \((\text{MoO}_4^{2-}, \text{WO}_4^{2-}, \text{VO}_3^-, \text{HCO}_3^-)\) able to react with hydrogen peroxide to provide oxidizing peroxo intermediates have been designed. Double-tailed catasurfs turned out to be "balanced" providing spontaneously three-phase microemulsion (\(\mu\)em) systems when mixed with an appropriate organic solvent and water, without addition of electrolyte or alcohol. "Balanced catasurfs" thus play the role of surfactant, cosurfactant and catalyst simultaneously, leading to three-phase \(\mu\)em systems with only three components. Fig. 1 shows the application of the three-phase \(\mu\)em reaction medium to the dark singlet oxygenation. The catalyst, \(\text{MoO}_4^{2-}\), is specifically localized at the water-oil interface of the middle phase \(\mu\)em where the generation of the oxidizing species, \(1\text{O}_2\), exclusively takes place.

Fig. 1. Dark singlet oxygenation of a substrate \(S\) in a three-phase microemulsion system based on \([((\text{C}_8\text{C}_m\text{N}((\text{C}_1)_2)_2)\text{MoO}_4/\text{AcOtBu}/\text{water}]\) at 25°C.

The aqueous phase behavior of the catasurfs (\(T_{\text{Krafft}}, \text{cmc}, \text{liquid crystals formation}) has been determined and their efficiency to form \(\mu\)ems was studied using the so-called Fish diagrams. They could be compared in terms of both their \(C^*\) value, i.e. the minimal amount to form a single-phase \(\mu\)em and to their PACN value (Preferred Alkane Carbon Number), i.e. the EACN of the oil providing the optimal formulation at 25 °C. All these physico-chemical properties have also been determined for the non catalytic quaternary ammonium surfactants \([\text{C}_8\text{C}_m\text{N}((\text{C}_1)_2)_2]X\) where \(X = \text{Cl, Br, F, NO}_3^-, \text{ClO}_4^-, \text{HSO}_4^-, \text{SCN, CH}_3\text{SO}_4^-, \text{CH}_3\text{COO, salicylate and SO}_4^{2-}\), which have been shown to match the Hofmeister series [1,2].

References: