

Program

Association in Solution III
Self-Assembly: From Bio-Colloids to Nano-Engineering

Bifröst University, Iceland

July 23-27, 2012

Conference Co-Chairs

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Monday July 23, 2012

16:00 – 17:00 Registration / Conference check-in

17:00 – 17:30 Coffee & tea

17:30 – 18:00 *Welcome and introductory remarks*
Ulf Olsson and Norman Wagner

Thermodynamics & intermolecular interactions – Chair: Norman Wagner

18:00 – 18:30 *Self-assembly at steady state*
Håkan Wennerström, Lund University, Sweden

18:30 – 19:00 *A general interaction potential for hydrophobic and hydrophilic interactions*
Stephen Donaldson, University of California Santa Barbara, USA

19:30 - Dinner

Notes

- *Technical sessions will be held in the Rauðbrók room*
- *Posters will be in the Hrifla room*
- *All meals will be in the Hátíðarsalur room*
- *Audiotaping, videotaping and photography of presentations are prohibited.*
- *Speakers – Please have your presentation loaded onto the conference computer prior to the session start (preferably the day before).*
- *Speakers – Please leave at least 5 minutes for questions and discussion.*
- *Please do not smoke at any conference functions.*
- *Turn your mobile phones to vibrate or off during technical sessions.*

Tuesday July 24, 2012

Colloids – Chair: Robert Prud'homme

- 08:30 – 09:00 *Charged rod-like colloids in electric fields*
Jan Dhont, Forschungszentrum Jülich, Germany
- 09:00 – 09:30 *Total internal reflection microscopy measurements of low refractive index particles in polar solvent mixture*
Johan Bergenholtz, University of Gothenburg, Sweden
- 09:30 – 10:00 *Tuning self-assembly, microstructure, phase separation and gelation with depletion interactions in suspensions of charged colloids*
Anna Stradner, Lund University, Sweden
- 10:00 – 10:30 Coffee & tea
- 10:30 – 11:00 *Anisotropic microparticles on fluid interfaces*
Kathleen Stebe, University of Pennsylvania, USA
- 11:00 – 11:30 *Assembling responsive nanoparticles*
Peter Schurtenberger, Lund University, Sweden
- 11:30 – 12:00 Poster program presentation
- 12:15 – 15:30 Lunch and discussions/poster session
- 15:30 – 16:00 Coffee & tea

Emulsions and micelles – Chair: Reinhard Strey

- 16:00 – 16:30 *Why are hydrophobic/water interfaces negatively charged?*
Kevin Roger, ESPCI Paris, France
- 16:30 – 17:00 *Tuning the shape and stoichiometry of self-assembled phospholipid nanodiscs*
Lise Arleth, University of Copenhagen, Denmark

Peptide self-assembly – Chair: Masayuki Imai

- 17:00 – 17:30 *Self-assembled nanotubes in a model peptide system*
Ulf Olsson, Lund University, Sweden
- 17:30 – 18:00 Break
- 18:00 – 18:30 *Functional nanotubes from the self-assembly of peptide/polymer conjugates*
Sebastian Perrier, University of Sydney, Australia
- 18:30 – 19:00 *Engineering amyloid fibril structure and function via controlled protein aggregation*
Raffaele Mezzenga, ETH Zürich, Switzerland
- 19:30 - Dinner

Wednesday July 25, 2012

Surfactant self-assembly – Chair: Gregory Warr

- 08:30 – 09:00 *Dilute aqueous gel networks containing fatty alcohol and surfactant*
Claudia Schmidt, University of Paderborn, Germany
- 09:00 – 09:30 *Phase behavior of microemulsions with weak and strong surfactants*
Doris Vollmer, Max Planck Institute, Mainz, Germany
- 09:30 – 10:00 *How to make nanofoams*
Reinhard Strey, University of Cologne, Germany
- 10:00 – 10:30 Coffee & tea

Self-assembly kinetics – Chair: Michael Gradzielski

- 10:30 – 11:00 *Probing self-assembly processes in bulk and at interfaces using
synchrotron scattering techniques*
Diego Pontoni, ESRF Grenoble, France
- 11:00 – 11:30 *Kinetic self-assembly of block copolymers during rapid precipitation*
Robert Prud'homme, Princeton University, USA
- 11:30 – 12:00 *Kinetics in surfactant solutions studied by combining stopped-flow
mixing with synchrotron SAXS*
Jan Skov Pedersen, Aarhus University, Denmark
- 12:15 – 18:00 Lunch and excursions
- 18:00 – 19:00 Poster session
- 19:30 - Dinner

Thursday July 26, 2012

Bio-membranes – Chair: Jan Dhont

- 08:30 – 09:00 *Reversible gelation of vesicles, colloidal particles and biological cells*
Srinivasa R. Raghavan, University of Maryland, USA
- 09:00 – 09:30 *Exploring the energetics governing cholesterol homeostasis*
Paul Butler, NIST, USA
- 09:30 – 10:00 *Anomalous lateral diffusion in a viscous membrane surrounded by viscoelastic media*
Shigeyuki Komura, Tokyo Metropolitan University, Japan
- 10:00 – 10:30 Coffee & tea

Bio-engineering – Chair: Alex Evilevitch

- 10:30 – 11:00 *DNA-lipid complexes: structure and Brownian motion*
Frederic Nallet, University of Bordeaux, France
- 11:00 – 11:30 *Short DNA (sDNA) stacking regulates a thermotropic cubic to hexagonal phase transition in sDNA-lipid assemblies*
Cecilia Leal, University of Illinois, Urbana-Champaign, USA
- 11:30 – 12:00 *Phospholipids and proteins as active components of transistors: Where soft matter and organic electronics meet*
Gerardo Palazzo, University of Bari, Italy
- 12:15 – 15:30 Lunch and discussions/poster session
- 15:30 – 16:00 Coffee & tea

Viscoelastic assemblies – Chair: Kathleen Stebe

- 16:00 – 16:30 *Non-equilibrium association between oppositely charged polyelectrolytes and surfactants in the absence and presence of different additives*
Róbert Mészáros, Eötvös Loránd University, Hungary
- 16:30 – 17:00 *Structure and dynamics of highly viscous polyelectrolyte-surfactant complexes*
Michael Gradzielski, Technical University of Berlin, Germany
- 17:00 – 17:30 *Structural signature of a brittle-to-ductile transition in self-assembled networks*
Christian Ligoure, University of Montpellier II, France
- 17:30 – 18:00 Break
- 18:00 – 18:30 *Lamellar-“onion”-lamellar transition with varying temperature under shear flow in nonionic surfactant/water systems*
Tadashi Kato, Tokyo Metropolitan University, Japan
- 18:30 – 19:00 *In situ large amplitude oscillatory shear (LAOS) experiments on rod-like viruses and colloidal platelets*
Pavlik Lettinga, Forschungszentrum Jülich, Germany
- 19:30 - Dinner

Friday July 27, 2012

Self-assembly in ionic liquids - Chair: Ulf Olsson

- 08:30 – 09:00 *Amphiphilic structure and solubility in ionic liquids*
Gregory Warr, University of Sydney, Australia
- 09:00 – 09:30 *Self-assembly of cationic surfactants and block copolymers in protic ionic liquids*
Norman Wagner, University of Delaware, USA
- 09:30 – 10:00 Coffee & tea

Colloidal Biology - Chair: Lise Arleth

- 10:00 – 10:30 *Lambda-phage DNA confined by lipid membranes: Soft strings against soft surfaces*
Carlos Marques, Institut Charles Sadron, Strasbourg, France.
- 10:30 – 11:00 *Physical chemistry of viral evolution*
Alex Evilevitch, Carnegie Mellon University, USA,
and Lund University, Sweden
- 11:00 – 11:30 *Molecular assembly to protocell*
Masayuki Imai, Tohoku University, Japan
- 11:30 – 12:00 *Concluding remarks*
Håkan Wennerström and Kathleen Stebe
- 12:15 – Lunch and departure

Abstracts

**Association in Solution III
*Self-Assembly: From Bio-Colloids to Nano-
Engineering***

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Engineering Conferences International

SELF-ASSEMBLY AT STEADY STATE

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At the interface between air and an aqueous solution there is typically a non-equilibrium situation with water constantly evaporating. There is a gradient in the chemical potential of the water. Air at 50% relative humidity, which is typical ambient conditions, corresponds to very dry conditions. For systems prone to self-assemble the gradient in the chemical potential of the water can extend somewhat into the solution. This can in turn give rise to self-assembly structures at the interface not found in the bulk. We will present a formalism, based on the diffusion equation, that describes the basic principles of the phenomenon. The formalism will then be applied to specific two and three component systems illustrating a range of effects that might be observed at the surface of an aqueous system exposed to dry air.

A GENERAL INTERACTION POTENTIAL FOR HYDROPHOBIC AND HYDROPHILIC INTERACTIONS

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Hydrophobic interactions, driven by the inability of water molecules to hydrogen bond in the vicinity of hydrophobic molecules and surfaces resulting in strong, long range attractive interactions between hydrophobic moieties, are ubiquitous in the self-assembly of complex structures and many physical and biological processes, such as protein folding, bio-membrane adhesion and fusion, and drug-delivery vehicles. Hydrophilic interactions are similarly ubiquitous. Hydrophilic molecules or surfaces have several layers of strongly bound water molecules, which become increasingly more difficult to dehydrate as the water gap decreases, resulting in a strongly repulsive hydration interaction. A quantitative, theoretical description of both interactions has remained elusive, especially in cases where both interactions determine the final self assembled state, such as heterogeneous surfaces common in protein folding, bio-membranes and detergent action. Recent surface forces apparatus (SFA) measurements allowed us to obtain a hydrophobic interaction potential, and the model quantitatively captures the long range forces, short range forces, breakthrough point, and final hydrophobic adhesion as two bilayers approach, spread (thin), rupture, hemi-fuse, and are then separated from adhesive contact. These results indicate that the hydrophobic interaction depends on the interfacial tension ($\gamma_i \sim 50$ mJ/m²) and excess exposed hydrophobic area (which increases as the bilayer is stressed), with an exponential decay with a decay length of 1 nm. More recent analysis has shown that our model can also apply to the case of excess *hydrophilic* area, and quantitative agreement with previous surface forces experiments is obtained, with an identical decay length and pre-exponential factor. A new picture is emerging, which suggests both water-based interactions can be described by a single unifying equation, and perhaps indicates a similar mechanism for both interactions: for example, increased water density (and/or hydrogen bonding order parameter) near hydrophilic surfaces, and depleted water density (and a corresponding decrease of the order parameter) near hydrophobic surfaces.

CHARGED ROD-LIKE COLLOIDS IN ELECTRIC FIELDS

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Concentrated suspensions of long and thin, stiff rods (fd-virus particles) at low ionic strengths are found to exhibit various phases and dynamical states under external electric fields, depending on the field amplitude and frequency. A non-chiral nematic, a chiral nematic and a homeotropically aligned homogeneous phase are observed, and a dynamical state where non-chiral nematic domains melt and form. These phases and dynamical states are the result of interactions between polarized double layers, polarized layers of condensed ions and/or electro-osmotic flow. The phase/state diagram drastically changes around 1 kHz, where polarization charges become insignificant, and the only stabilizing mechanism is related to hydrodynamic interactions resulting from electro-osmotic flow. Non-equilibrium critical phenomena are found in the sense that a length scale and time scale diverge on approach of a specific point in the phase/state diagram.

TOTAL INTERNAL REFLECTION MICROSCOPY MEASUREMENTS OF LOW-REFRACTIVE-INDEX PARTICLES IN POLAR SOLVENT MIXTURES

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The interactions between colloidal microspheres and plane walls have been studied in different solvents using total internal reflection microscopy (TIRM). Particles, comprising a polystyrene core surrounded by a layer of fluorinated polymer, were synthesized to be responsive in terms of the van der Waals interaction to changes in the refractive index of the solvent. In principle, with a proper selection of the refractive index of the solvent and provided the polystyrene-wall interaction is weak, it should be possible to turn the van der Waals interaction from an attraction to a repulsion even in polar solvent mixtures. The measurements show that matching the refractive index of the fluorinated particle shell exposes an attraction as the electrostatic repulsion is progressively screened by added salt. For a refractive index between those of the plane wall and fluorinated particle shell, the results can be qualitatively rationalized by a longer-range repulsive van der Waals interaction. However, the particle can be attached irreversibly to the wall, presumably due to the van der Waals interaction exhibiting a deep attractive minimum for the smallest separations where screening of the static contribution to the Hamaker constant becomes ineffectual.

TUNING SELF ASSEMBLY, MICROSTRUCTURE, PHASE SEPARATION AND GELATION WITH DEPLETION INTERACTIONS IN SUSPENSIONS OF CHARGED COLLOIDS

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Phase separation and dynamical arrest in suspensions of colloids with short-range attractions has attracted considerable attention in the soft matter community. Numerous studies have demonstrated the presence of solid-like structures such as particle gels or colloidal glasses under conditions where attractions are large enough to trigger phase separation. Particularly interesting are systems where mixed potentials, i.e. a combination of a short-range attraction and a long-range soft repulsion, exist. Under these conditions additional states such as equilibrium cluster phases and cluster glasses can exist. While these investigations have been mainly triggered by attempts to make and exploit analogies between the resulting phase or state diagrams of colloidal suspensions and atomic and molecular systems, phase separation and dynamical arrest are topics that are of particular importance in areas such as materials and food science.

Here we demonstrate how we can tune the interaction potential and the resulting phase behavior and the microstructure of the states that form by using a combination of a well-defined colloid with tunable charge density and an added water-soluble polymer. We first show how we can make an appropriate model colloid through the synthesis of a core shell particle with a polystyrene core and an added mixed shell that provides electrosteric stabilization. We then show how we can tune the resulting mixed potential through appropriate variations of the ionic strength and polymer concentration. We describe the resulting plethora of equilibrium and non-equilibrium states as a function of the strength and range of the two dominating contributions to the mixed potential, the depletion induced attraction and the soft screened Coulomb repulsion. We compare the experimentally determined phase diagrams with theoretical predictions and characterize the resulting microstructures and their dynamics through a combination of spin-echo small-angle neutron scattering (SESANS), small-angle neutron (SANS) and x-ray (SAXS) scattering and diffusing wave spectroscopy over a large range of length and time scales.

ANISOTROPIC MICROPARTICLES ON FLUID INTERFACES

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When microparticles with complex shapes are placed on the interface of an isotropic liquid, they interact owing to capillarity to form regular structures. On curved interfaces, particles migrate owing to capillarity to sites of high curvature. We have demonstrated this phenomenon using interfaces with imposed curvature fields molded by confining geometries. When such microparticles are placed at interfaces of nematic liquid crystals, the elastic energies in the liquid crystalline subphase influence the particle trajectories and the structures formed. Recent progress in understanding particle migration and assembly in defect arrays defined by confining geometries is presented.

ASSEMBLING RESPONSIVE NANOPARTICLES

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It is clear that the design and fabrication of future materials and devices for photonics, molecular electronics, or drug delivery will enormously benefit if we are capable of self-assembling nanoparticles into synthetic nanostructures with the precision and reliability found in biological self-assembly. However, this requires control over their assembly into precise and predictable structures, which still remains the primary obstacle to the bottom-up construction of novel materials and devices. It can only be achieved if we understand the relationship between specific types of interactions and the resulting target structures, and subsequently develop the capability to engineer and control these interactions between the different building blocks. Progress in soft matter based materials science and nanotechnology thus critically depends on a sound understanding of the various intermolecular interactions acting in often highly complex systems.

It is here where responsive nanoparticles such as thermo- or pH-sensitive microgels or magnetic hybrid particles are ideal model systems to investigate the relationship between interactions and self-assembled structures. They allow for a variation of the form, strength and range of the interaction potential almost at will. They are not only attractive models in basic research, but also of considerable technological importance to materials science and nanotechnology as building blocks for nanostructured responsive organic-inorganic hybrid systems. Here we will demonstrate how we can design and synthesize functionalized responsive nanoparticles that can be used to make adaptive polymer-colloid nanomaterials with tailored optical, magnetic and mechanical properties. We will in particular describe how we can use the thermo-response of a microgel shell to achieve an active control of the volume fraction and the interaction potential between core-shell particles in order to induce controlled particle self-assembly into crystalline or glassy structures and reversibly cycle through different phase transitions in order to explore the rich variety of structures that exist in dense suspensions. We will show how we can create anisotropic interactions through the use of external electric or magnetic fields. A particular emphasis will be given to the possibilities of fabricating photonic crystals with tunable optical properties.

WHY ARE HYDROPHOBIC/WATER INTERFACES NEGATIVELY CHARGED?

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Materials that are dispersed at nanometric scales have large areas of interface, and therefore hold a substantial amount of interfacial energy. In the case of liquid/liquid dispersions, the interfaces will therefore recombine unless some adsorbed species block the recombination processes. Accordingly, the stability of emulsions is usually controlled with the use of amphiphilic molecules, macromolecules, or else particles that bind to the interfaces and prevent their recombination. The mechanisms by which metastability is achieved are well understood.

However emulsions made of pure oil in pure water have also been found to be metastable in the absence of any added stabilizer. The droplets of these surfactant-free emulsions are negatively charged and the surface charge density increases in a typical fashion with pH. The most frequent explanation given for this phenomenon is that hydroxide ions adsorb at hydrophobic-water interfaces. However, this interpretation raises a number of difficulties, as it requires adsorption energies for hydroxide ions above 20 times the thermal energy kT . It would also imply an outstanding selectivity for the hydroxide ions, compared to other anions that do not bind at such interfaces, which contradicts the well-known Hoffmeister behaviour.

We solve that problem by challenging the experimental feasibility of pure water/hydrophobic interfaces. We use a solvent-shifting method to produce fine emulsions with large surface areas and droplet sizes that can be easily controlled according to the amount of stabilizer. We show that the oils, even at a purity of 99% and 99.8%, contain weak acids. We demonstrate that the resulting surface charge density decreases with increasing oil purity, at a constant hydroxide ions concentration. We observe that the deliberate contamination of high purity oils with fatty acids reproduces the behaviour of lower purity oils. The pH-dependence of the surface charge density quantitatively corresponds to the titration curve of fatty acids at an interface.

We conclude that hydrophobic interfaces with water are charged through the acid-base reaction of hydroxide ions with traces of fatty acids, with a reaction free energy around $20kT$. This conclusion offers new opportunities to tune bottom-up routes for making nanomaterials through self-assembly, such as solvent-shifting methods.

TUNING THE SHAPE AND STOICHIOMETRY OF SELF-ASSEMBLED PHOSPHOLIPID NANODISCS

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Phospholipid nanodiscs have quickly become a very widely used platform for functional studies of membrane proteins and several research groups are now investigating the system with the aim of developing it into a platform for structural studies of membrane proteins. Many of these projects are however challenged by a poor control of the molecular self-assembly process that ultimately should center a membrane protein inside the nanodisc. In a recent study, a combined small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) allowed for extracting detailed structural information about the nanodiscs in terms of e.g. their over-all shape - this was shown to be elliptical - and the packing of the lipids within the nanodiscs in terms of the local areas per headgroup. In an attempt to further understand the nanodisc self-assembly process and this way contribute to obtaining better control of the membrane protein incorporation, the self-assembly process of POPC:MSP1D1 nanodiscs have been systematically modulated and the detailed structure of the resulting nanodiscs have been determined using the previously developed small-angle scattering based approach. We investigate the effect of varying the the removal speed of the reconstitution detergent, the lipid:belt stoichiometry of the reconstitution mixture, as well as the detergent type used in the reconstitution process. We find that, of the three factors, the detergent type plays the most significant role for the control of the shape and stoichiometry of the formed nanodiscs. Our data also clearly shows that the detergents optimal for solution storage and crystallization of membrane proteins are not necessarily the same as those giving rise to an optimal reconstitution. Based on our experiments we suggest that reconstitution strategies based on mixed detergent systems are not only convenient but also optimal when reconstituting membrane proteins into nanodiscs.

SELF-ASSEMBLED NANOTUBES IN A MODEL PEPTIDE SYSTEM

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Understanding peptide aggregation/self-assembly is important e.g. for peptide drug formulation and delivery and for its connection to a number of neurodegenerative diseases. Here we have studied the trifluoroacetate (tfa) salt of the simple model heptapeptide A6K (A=alanine, K=lysine) that self-assembles in water into micrometer long, hollow nanotubes with a remarkably monodisperse radius $R=26$ nm, above a critical aggregation concentration, c_{ac} (volume fraction), being 0.10 at room temperature. The aggregation is highly cooperative, and the c_{ac} shows only a weak temperature dependence consistent with a small negative enthalpy of aggregation of aggregation of ca. $-k_B T$ per molecule. The nanotube wall consists of a crystalline peptide monolayer, i.e. a cylindrically bent 2D crystal, involving a cross beta-sheet like arrangement of the peptide molecules. The nanotube formation in supersaturated solutions occurs through an initial nucleation and growth of monolayer sheets. The fragments can attach and connect to form larger structures, implying nanotube growth by "oriented attachment". In undersaturated conditions, the nanotubes dissolve from the ends. First into long disconnected peptide (beta-sheet?) threads, that then further dissolves into peptide monomers.

FUNCTIONAL NANOTUBES FROM THE SELF-ASSEMBLY OF PEPTIDE / POLYMER CONJUGATES

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Functional Nanotubes from the Self-Assembly of Peptide / Polymer Conjugates

Peptide–polymer conjugates capable of self-assembling to form ordered structures provide access to hierarchically ordered and functional soft materials with applications ranging from nanotechnology to tissue engineering.[1] β -sheet forming peptides are amongst the most versatile self-assembling peptide building blocks to form a range of nanostructures including fibrils, β -barrels, hollow β -helices and stacks of macrocycles.[2-7] The latter have been widely investigated following pioneering studies by Ghadiri and coworkers,[7] in which cyclic peptides comprising alternating L- and D- amino acids were shown to form self-assembled nanotubes with β -sheet-like antiparallel hydrogen-bonding interactions between the macrocycles.[8] Self-assembly of this type of cyclic peptide has been observed for peptides of 8-12 amino acids in length (providing nanotubes with diameters of 7 – 13Å) and found to be tolerant of a wide range of functional groups on the peptide side chains.

The conjugation of polymers to such cyclic peptides allows the self-assembly of well-defined polymer coated nanotubes,[9-14] which have enormous potential to be converted into functional materials. We have designed a convergent synthetic strategy where we ligate pre-made polymeric chains to cyclic peptide, then assemble the resulting conjugates into nanotubes. The control over polymeric chain length, functionality, solvent and external triggers such as temperature and pH permit us to control the length and thickness of the tubes. We exploit the control over dimensions and functionalities of these 'soft' nanotubes in applications ranging from drug delivery to nanopores.[12-14]

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ENGINEERING AMYLOID FIBRILS STRUCTURE AND FUNCTION VIA CONTROLLED PROTEINS AGGREGATION

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Aggregation of proteins is central to many aspects of daily life, ranging from food technology and pharmaceutical science, to blood coagulation and health disorders, such as sickle-cell disease, arterial thrombosis, or eye cataract formation. In particular, association of proteins into amyloid fibrils is a highly specific process occurring both in-vivo, such as in the Alzheimer, Parkinson or prion-related neurodegenerative diseases, and in-vitro, as in the case of processed food proteins.

In this talk I will discuss our recent contribution to the understanding of the association processes converting globular proteins into amyloid fibrils, with emphasis on β -lactoglobulin and lysozyme, which have both fundamental and practical relevance. I will first illustrate how the unique combination of experimental techniques (light, neutron and x-rays scattering, AFM and cryoTEM), with polymer and colloidal physics concepts, can reveal important structural features from the nanometer to micron lengthscales and how these information can be used to understand the main mechanisms ruling aggregation.

I will then address how these mechanisms can be engineered to produce highly ordered multistranded amyloid fibrils with tunable nanostructures, in which the number of protofilaments forming a single fibril, their topology, and the twisted ribbon, helical ribbon and nanotube polymorphism can be efficiently controlled.

Finally, I will also touch on how these protein fibrils can be exploited as unique building blocks for complex and functional fluids, serving fields as diverse as food science, biomaterials, biosensors and optoelectronics, and I will illustrate this via relevant examples for each specific category.

References

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DILUTE AQUEOUS GEL NETWORKS CONTAINING FATTY ALCOHOL AND SURFACTANT

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Dispersing small amounts of water-insoluble fatty alcohols and surfactants in water often results in materials of gel-like consistency. These gels, which can be used for cosmetic or pharmaceutical lotions and creams, are often non-equilibrium multiphase systems, containing a network of mixed surfactant/alcohol crystals and liquid crystalline aggregates. To optimize manufacturing conditions it is important to understand how the physicochemical properties of the gel and its long-time stability are related and how they can be controlled. One important parameter is the dynamic state of the alkyl chains, which can be solid or liquid-like. Using dilute mixtures of sodium dodecyl sulfate (SDS), cetyl alcohol (CA) and D₂O [1] as a model we will demonstrate that NMR spectroscopy is a useful tool for the investigation of the gels. Using high resolution ¹H NMR the alcohol and the surfactant molecules with liquid-like dynamics can be selectively detected, whereas molecules in the solid state give no signal. Temperature-dependent NMR spectra of mixtures containing varying ratios of surfactant and fatty alcohol at constant water content of 97 wt. % have been investigated. We find that the NMR signals from the α and β CH₂ groups of alcohol and surfactant can be clearly distinguished. From the intensities of these signals relative to reference solutions the liquid fractions of alcohol and surfactant can be determined. In addition, the peak shapes yield information on the type of aggregates. Small micelles exhibit well-resolved multiplets due to J couplings, whereas larger aggregates result in broadened peaks without fine structure. At high SDS concentrations the mixtures form micellar solutions of low viscosity and the alcohol is solubilized in the micelles. On the other hand, at high alcohol concentrations the samples have a gel-like consistency. In this case the alcohol chains are rigid at room temperature. At intermediate alcohol concentrations phase separation occurs. The NMR results are compared with those obtained by other methods, such as differential scanning calorimetry, neutron scattering, and TEM, to complete the picture of the phase structures.

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PHASE BEHAVIOR OF MICROEMULSIONS WITH WEAK AND STRONG SURFACTANTS

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Microemulsions are thermodynamically stable isotropic mixtures of water, oil and surfactant with unique properties like ultralow interfacial tension, large interfacial area and the ability to solubilise other immiscible liquids. Depending on temperature and concentration, surfactant molecules associate into a micellar, lamellar, hexagonal or sponge like bicontinuous structure. The local curvature of the surfactant molecule largely determines the structure of microemulsions. Microemulsions can have three different macroscopic phases: isotropic or 1 ϕ ; 2 ϕ with oil/ water emulsified out of the microemulsion; 3 ϕ with oil and water emulsified out of the microemulsion [1]. A quantitative prediction of the phase diagram of non-ionic microemulsion is presented here. Due to the conservation of the components, in a 1 ϕ the droplet size is determined by composition, whereas in 2 ϕ it is determined by temperature due to the temperature dependence of the spontaneous curvature $c_0(T)$. The dependency of the droplet size on $c_0(T)$ can be explained with Helfrich bending free energy density. However this approach cannot account for the 3 ϕ region. Therefore we proposed a modified Helfrich equation describing all the three macroscopic phases. It assumes that within a well-defined temperature interval two spontaneous curvatures coexist. To investigate the validity of this assumption we investigate the phase boundaries by differential scanning microcalorimetry. Spontaneous curvature plots calculated from fitting the emulsification boundaries sheds light to the coexistence of two curvatures over a wide range of temperature and surfactant concentration. Experimentally determined values for the phase transition temperatures and specific heat have been successfully fitted to the unified model [2]. [1] M. Kahlweit, R.Strey and G.Busse, Phys. Rev. E 47 (1993), 4197-4209. [2] H. Paroor, D.Vollmer, in preparation

HOW TO MAKE NANOFOAMS

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Polymeric nanofoams are difficult to make posing both scientific and technological challenges. Their low thermal conduction and their optical transparency promise advantageous technical applications. In particular the much improved thermal insulation is an important aspect of high economic and environmental importance. To date no cost-efficient processing method for the production of such nanofoams has been provided. In the past decade we have developed various strategies to achieve this goal. One approach is to formulate o/w microemulsions, normally mixtures of oil droplets in water, where the 'water' is built by from components that form the polymeric matrix, e.g. a melamine resin, where the 'oil' is a supercritical fluid e.g. CO₂ and appropriate surfactants. The clue is that after initiating the polymerisation a simple pressure release leads to an unhindered expansion of the 'oil' droplets to gas bubbles which together with the solidifying matrix form a nanofoam. Hence we called this procedure 'Principle of Supercritical Microemulsion Expansion, POSME'. For polyurethane foams this procedure has been adapted and the judicious choice of the components needed recently published. However, for non-polar matrices this approach not applicable. Here we developed very recently an alternative, still undisclosed procedure that will be explained.

PROBING SELF-ASSEMBLY PROCESSES IN BULK AND AT INTERFACES USING SYNCHROTRON SCATTERING TECHNIQUES

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This presentation will give an overview of new possibilities offered by synchrotron X-ray scattering techniques in the investigation of nano-scale structure and non-equilibrium dynamics of self-assembled soft matter systems. Self-association of amphiphilic molecules and nanoparticles (NPs) in bulk, and at liquid/liquid or solid/liquid interfaces play a fundamental role in engineering novel nano-materials. The detailed structural characterization of such self-assembled nanostructures and interfaces is essential for reaching a deeper understanding of their fundamental physics as well as predictive capabilities of the underlying association processes.

Particular emphasis will be devoted to surfactant-modified hydrophobic interfaces [1], surfactant-induced interfacial NP self-association, and the restructuring of solid-supported NP monolayers via controlled wetting [2]. Self-assembly in bulk solutions will be demonstrated by investigations of the spontaneous formation of unilamellar vesicles upon rapid mixing of two oppositely charged surfactant solutions [3]. Millisecond time-resolved experiments probe the pathways of the self-assembly and reveal variety of transient intermediate structures depending on the initial concentrations of the surfactant solutions [4]. The same final structure can be reached by different routes, therefore time-resolved scattering experiments are essential to capture transient states and probe their dynamics.

The talk will end with a brief presentation of the Partnership for Soft Condensed Matter being established in Grenoble (France), for providing enhanced user support to soft matter scientists interested in using neutrons and synchrotron to unravel the structural and dynamical properties of bulk and interfacial soft matter systems.

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KINETIC SELF-ASSEMBLY OF BLOCK COPOLYMERS DURING RAPID PRECIPITATION

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With widespread interest in the generic “nano”, attention has been focused on strategies of making small particles. High-value applications that drive new process innovation include very hydrophobic pharmaceutical actives, dyes and pigments for ink jet printing, or the dispersal of highly toxic insecticides on carriers. While it is relatively easy to make inorganic nano-particles, for example CdS particles, it is much more challenging to make nanoparticles from low surface energy organic solids. Strategies for forming nano particles vary from supercritical spraying, supercritical freezing, milling, solvent exchange precipitation, and imbibing into polymeric micelles. The solute and process combine to give differences in crystalline/amorphous products, individual particles/agglomerates, and uniformity/polydispersity of sizes. We have developed a new technology that has two components: (1) rapid and tailored micromixing in an impinging jet, and (2) novel block copolymer stabilizers. The impinging jet process allows the production of nano-particles by: 1) elimination of mass transfer limitations and compositional gradients within 10 ms as determined by independent measurements with competitive-parallel reactions, 2) production of high supersaturations and solute concentrations so that high production rates can be obtained, and 3) control of particle size by stabilization of the particle using block copolymer self-assembly. The process depends critically on control of three time scales: particle nucleation and growth, block copolymer micellization, and polymer adsorption on the particle to produce steric stabilization. We present data on characterization of the mixing times using competitive reactions, data on polymer micellization kinetics, and results on the successful production of β -carotene and paclitxel particles with control of the particle size between 40 nm to 600 nm. A range of block copolymers have been used : PS-b PEO, PBA-b-PAA, and PCL-b-PEO. Homogeneous rapid nucleation and growth produces particle size distributions that are much narrower than those obtained by alternate size-reduction or precipitation routes, and results in a decreased tendency to Ostwald ripen. The kinetics of assembly and reorganization in the nanoparticle core will be highlighted.

KINETICS IN SURFACTANT SOLUTIONS STUDIED BY COMBINING STOPPED-FLOW MIXING WITH SYNCHROTRON SAXS

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Surfactant solutions are self-assembled systems that rearrange as a response to changes in the environment. High brilliance synchrotron beamlines allow in situ SAXS studies of kinetics of the structural changes with millisecond time resolution. Here we present novel examples of application of synchrotron SAXS in combination with the stopped-flow technique for studying fast transitions in surfactant solutions. In the first example, formation of dodecyl maltoside (DDM) micelles from singly dissolved surfactants in dimethylformamide upon rapid mixing with water is studied. Water decreases the critical micelle concentration and induces micelle formation. The complete process could be followed by SAXS, and all data frames could be modeled by a combination of scattering from singly dissolved surfactant molecules and an increasing fraction of ellipsoidal micelles. The results were interpreted within a mechanistic framework, describing the process as a series of insertion/expulsion events of single molecules. In two other systems, transitions from globular to cylindrical micelles were studied. In one system the transition was induced by mixing solutions of globular sodium dodecyl sulphate (SDS) micelles with a salt solution. This leads to screening of the repulsion between the charged SDS headgroups, giving a lower preferred surface curvature and a very fast transition to cylindrical micelles. In another system the transition was induced by mixing a solution of globular SDS micelles with a solution of globular DDM micelles. The mixing leads to a reduction of electrostatic repulsion between the SDS headgroups and a more effective packing of the sterically small SDS headgroups and the bulky DDM headgroups. Both effects give a lower preferred surface curvature and result in a two-step transition to cylindrical micelles.

REVERSIBLE GELATION OF VESICLES, COLLOIDAL PARTICLES, AND BIOLOGICAL CELLS

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This talk will discuss the action of associating polymers, i.e., polymers with hydrophobic stickers attached to a hydrophilic backbone, on various types of nano or microstructures. In particular, we have conducted extensive studies with a hydrophobically modified (hm) derivative of the cationic polysaccharide, chitosan. When hm-chitosan is combined with a solution of vesicles, the hydrophobes get embedded in the hydrophobic interiors of vesicle bilayers. In turn, the vesicles are connected by polymer chains into a three-dimensional gel network that exhibits elastic rheology. In contrast, the native polymer (without hydrophobes) does not produce a gel. Recently, we have found that similar gelation can also be induced by combining hm-chitosan with a variety of colloidal particles, including carbon microspheres, polystyrene latex, and laponite. Again, the presence of hydrophobes is found to be essential for gelation and it is thought that the hydrophobes are adsorbed on the surfaces of these particles. Lastly, gelation due to hm-chitosan also occurs for a range of biological cells, including blood. The ability to gel blood suggests the use of hm-chitosan as a hemostatic agent, i.e., to arrest bleeding from serious wounds. Indeed, we have now conducted a range of experiments with animal models that confirm the hemostatic ability of this polymer. In all the above cases and especially with blood, it is useful to have the capability of reversing the polymer-induced gelation. We have found that gelation can indeed be reversed by the addition of alpha-cyclodextrin, a sugar-based supramolecule with a hydrophobic binding pocket. The reversal occurs because hydrophobes detach from blood cells and embed within the pocket of the cyclodextrin. Overall, the scheme for reversible gelation discussed here is likely to prove useful in a variety of applications.

EXPLORING THE ENERGETICS GOVERNING CHOLESTEROL HOMEOSTASIS

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Cholesterol is an important structural component of most cell membranes contributing to their organization, dynamics, and bending modulus; regulating their interactions with the cytoskeleton; and in some cases controlling the functions of membrane proteins crucial for several trans-membrane signaling processes. Healthy cells maintain a cholesterol gradient along the exocytic path from the endoplasmic reticulum (ER) to the plasma membrane. Dysfunction in cholesterol movement plays a key role in atherosclerosis and heart disease, and has been implicated in dementias (such as Alzheimer's), diabetes and cancer, as well as in several rare but fatal diseases. This importance of cholesterol transport within the cell has led to numerous studies, however progress has been hampered by the wide variability in reported values for intra- and inter-membrane transport rates.

In order to address this important long standing issue we have undertaken a series of studies using Time-Resolved Small Angle Neutron Scattering (TR-SANS) as an in situ probe of cholesterol transfer rates in the absence of chemical tags or extraneous compounds. In the past decade, TR-SANS has been successfully applied to study the exchange rate of polymer chains between polymer micelles and more recently to study the residence time of lipids within a vesicle. By judicious use of deuterated lipids and contrast matching techniques we can observe the distribution and redistribution of cholesterol within the otherwise invisible vesicle hosts. Interestingly, in the pure POPC system the cholesterol flipping rates are slow enough to limit the exchange and can thus be deduced as well. By measuring the kinetic rate constants at several temperatures we extract the energies of activation for these processes. Our controversial results reveal dramatically slower transport kinetics than current believed, particularly for intra-membrane flipping where our measured rates are several orders of magnitude slower. Further we have shown how the presence of various chemical tags and extraneous compounds employed in traditional kinetic measurements can significantly affect the system thermodynamics, (accelerating cholesterol transport rates by an order of magnitude), as does the nature and type of lipids forming the membrane (e.g. POPS, a lipid highly enriched in the inner leaflet of the plasma membrane) and the sterols being studied. We will discuss these results in the context of the very similar but far less controversial studies of pure lipid transport rates along with preliminary MD simulation results.

ANOMALOUS LATERAL DIFFUSION IN A VISCOUS MEMBRANE SURROUNDED BY VISCOELASTIC MEDIA

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Biomembranes are thin two-dimensional fluids which separate inner and outer environments of organelles in cells. We discuss the dynamics and responses of membranes when their surrounding solvent is viscoelastic rather than purely viscous. This is a common situation in all eukaryotic cells whose cytoplasm is a soup of proteins and organelles, including a thick sub-membrane layer of actin-meshwork forming a part of the cell cytoskeleton. We first obtain the generalized frequency-dependent mobility tensor and focus on the case when the solvent is sandwiched by hard walls. Due to the viscoelasticity of the solvent, the mean square displacement of a disk embedded in the membrane exhibits an anomalous diffusion. An useful relation which connects the mean square displacement and the solvent modulus is provided. We also calculate the cross-correlation of the particle displacements which can be applied for two-particle tracking experiments.

DNA-LIPID COMPLEXES: STRUCTURE AND BROWNIAN MOTION

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Structural and dynamic properties of a complex of hydrated DNA rod-like fragments dispersed in a non-cationic lipid mixture are described. At low hydration, the self-assembly process leads to highly ordered lamellar structures that have been characterized by combining X-ray scattering, optical microscopy, and freeze-fracture transmission electron microscopy. We observe a significant increase of the smectic order as DNA is incorporated into the water layers of the lamellar host phase. The effect of confinement on DNA ordering is investigated by varying the water content. A rich polymorphism is found, ranging from weakly correlated DNA-DNA in-plane organizations to highly-ordered structures, where trans-membrane correlations lead to the formation of columnar rectangular and columnar hexagonal superlattices of nucleotides embedded between lipid lamellae.

Using Fluorescence Recovery After Photo-bleaching on a confocal microscope, we investigate the Brownian motion of the DNA fragments in the anisotropic phase where DNA exhibits a local nematic symmetry, i.e. at intermediate hydrations. The height of the measurement volume ensures the averaging of the anisotropy of the in-plane diffusive motion parallel or perpendicular to the local nematic director in homeotropically-aligned lamellar domains. Still, as shown in using a model specifically designed to handle such a situation and predicting a non-Gaussian shape for the bleached spot as fluorescence recovery proceeds, the two distinct diffusion coefficients of the 2D-confined DNA particles can be retrieved from data analysis.

SHORT DNA (SDNA) STACKING REGULATES A THERMOTROPIC CUBIC-TO-HEXAGONAL PHASE TRANSITION IN SDNA-LIPID ASSEMBLIES

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Lyotropic phases of amphiphiles are classical examples of self-assembly. Their structure is generally determined by amphiphile molecular shape and phase transitions are governed primarily by composition. In this presentation we will show recent synchrotron small-angle X-ray scattering studies that demonstrate a new paradigm for membrane shape control where the electrostatic coupling of charged membranes to sDNA, with tunable temperature-dependent end-to-end stacking interactions, enables switching between the inverse gyroid cubic structure (Q_{II}^G) and the inverted hexagonal phase (H_{II}^C). In addition, we will show an example of a Q_{II}^G lipid aggregate functionalized with a non-stacking nucleic acid-small interfering RNA (siRNA)- that conveys remarkable siRNA delivery to mammalian cells.

We acknowledge support by DOE-BES grant number DOE-DE-FG02-06ER46314 (interplay between membrane shape and DNA stacking), NSF DMR-1101900 (phase behavior), and NIH GM-59288. This work made use of the Central Facilities of the Materials Research Laboratory at UCSB which are supported by the MRSEC Program of the NSF under award no. DMR-1121053; a member of the NSF-funded Materials Research Facilities Network (www.mrfn.org). Cecília Leal was funded by the Swedish Research Council (VR) and in part by DOE-BES. The X-ray diffraction work was carried out at the Stanford Synchrotron Radiation Lightsource (SSRL) beam line 4.2. CRS acknowledges useful discussions with KAIST Faculty where he has a WCU (World Class University) Visiting Professor of Physics appointment supported by the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology grant No. R33-2008-000-10163-0.

PHOSPHOLIPIDS AND PROTEINS AS ACTIVE COMPONENTS OF TRANSISTORS: WHERE SOFT MATTER AND ORGANIC ELECTRONICS MEET

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Innovative field-effect transistor (OFET) realized through the full integration in the electronic device of bio-systems will be presented. The focus of this contribution will be on the functional bio-interlayer (FBI) OFET architecture [1, 2]. In the FBI-OFET a layer of phospholipids or proteins is placed between the gate-dielectric and the organic semiconductor of a bottom-gate top-contacts OFET. This architecture directly interfaces supported biological layers to a OFET channel and strikingly, both the electronic properties and the bio-interlayer functionality are fully retained. Phospholipid and bacteriorhodopsin integrating OFETs exhibit marked electronic responses at clinically relevant volatile-anesthetic concentrations. This result challenges the current anesthetic action model relying on the so far provided evidence that doses much higher than clinically relevant ones (2.4%) do not alter lipid bilayers structure, significantly. Furthermore, a streptavidin embedding OFET shows label-free biotin electronic detection at 10 part-per-trillion concentration level, reaching state-of-the-art fluorescent assay performances. These examples show how the proposed bio-electronic platform, besides resulting in extremely performing biosensors, can open to insights into biological relevant phenomena involving membrane weak interfacial modifications. Finally, perspectives on electrolyte gated OFETs with supported lipid bilayers [3] will be discussed.

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NONEQUILIBRIUM ASSOCIATION BETWEEN OPPOSITELY CHARGED POLYELECTROLYTES AND SURFACTANTS IN THE ABSENCE AND PRESENCE OF DIFFERENT ADDITIVES

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It is well-known that the nanoassemblies of oppositely charged polyelectrolytes and surfactants formed in aqueous medium can easily be kinetically arrested. This means that the extension of the two-phase concentration range as well as the size of the formed assemblies is crucially dependent on the preparation protocol of the polyelectrolyte/surfactant mixtures. These nonequilibrium features have been recently interpreted by the formation of kinetically stable colloidal dispersions both at low and high surfactant-to-polyelectrolyte ratios within the transparent composition region of these systems [1-2]. Specifically, it has been shown that the precipitation may be prevented in a wide concentration range through hindering the aggregation of the polyelectrolyte/surfactant nanoparticles formed at the intermediate stage of the phase separation process [1-2]. In this case the mixtures are trapped in the nonequilibrium colloidal dispersion state. Depending on the solution mixing methods as well as on the presence of various additives, electrostatic and/or steric stabilization of these polyelectrolyte/surfactant dispersions could also be attained [3-4]. In the present contribution, the potential impact of different additives, such as electrolytes, uncharged polymers or nonionic surfactants, on the phase properties and nonequilibrium assembly formation of polyelectrolyte/surfactant systems is discussed.

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STRUCTURE AND DYNAMICS OF HIGHLY VISCOUS POLYELECTROLYTE/SURFACTANT COMPLEXES

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Mixtures of oppositely charged polyelectrolyte and surfactant exhibit rich phase behaviour and high structural diversity, depending on the mixing ratio, total concentration and molecular structure of the components. The self-assembled structures formed may extend over a large size range and have many potential applications, e.g. in cosmetics, detergency, drug delivery, and also for rheological control.

In our experiments mixtures of cationic polyelectrolyte JR400 with anionic surfactants (SDS, SDBS, SDES) were studied in the semi-dilute regime. In the range of excess polymer charges upon surfactant addition highly viscous networks are formed, where the viscosity increases by 3-4 orders of magnitude as compared to the pure polymer solution and the rheological properties of these systems were characterised comprehensively. The structure of the polyelectrolyte/surfactant complexes was studied by means of static and dynamic light scattering (SLS, DLS) and in further detail by means of small-angle neutron scattering (SANS). SANS with its option of contrast variation (using deuterated surfactant) provides a unique tool for obtaining a detailed structural picture. Our investigations show the formation of rod-like mixed aggregates whose length increases as a function of the surfactant concentration and these rods then become increasingly interconnected.

To get further insight into the relations between mesoscopic structure and dynamics and the macroscopic rheology, neutron spin-echo (NSE) were done which allow to probe the mesoscopic dynamics. Together with the DLS experiments, which probe larger length scales and can be described in terms of the mode-coupling theory, this yields a deeper insight into the complex dynamics of such complexes. Interestingly, NSE measurements show a much less pronounced effect on the dynamics as compared to DLS.

In summary, we studied the behaviour of oppositely charged polyelectrolyte/surfactant complexes in solution by correlation the pronounced viscous properties with the mesoscopic structure and dynamics. In particular we focussed here on the role of the polyelectrolyte in these complexes. These investigations are not only of fundamental interest but may also be valuable for the design of application formulations with tailor-made properties.

STRUCTURAL SIGNATURE OF A BRITTLE-TO-DUCTILE TRANSITION IN SELF-ASSEMBLED NETWORKS

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We study the nonlinear rheology of a novel class of transient networks, made of surfactant micelles of tunable morphology reversibly linked by block copolymers. We couple rheology and time-resolved structural measurements, using synchrotron radiation, to characterize the highly nonlinear viscoelastic regime. We propose the fluctuations of the degree of alignment of the micelles under shear as a probe to identify a fracture process. We show a clear signature of a brittle-to-ductile transition in transient gels, as the morphology of the micelles varies, and provide a parallel between the fracture of solids and the fracture under shear of viscoelastic fluids.

LAMELLAR/ONION/LAMELLAR TRANSITION WITH VARYING TEMPERATURE UNDER SHEAR FLOW IN NONIONIC SURFACTANT/WATER SYSTEMS

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In the past two decades, much attention has been paid to the effects of shear flow on the structure of the lyotropic phase composed of amphiphiles. Among them, the most striking result may be the transition from the lamellar structure to the onion structure where all the space is filled by multilamellar vesicles alone [1]. Although the onion formation has been reported for various systems, conditions and mechanism for the transition have not yet been established.

A few years ago, we have found the lamellar-to-onion transition with increasing temperature under a constant shear rate in a binary system of a nonionic surfactant C16H33(OC2H4)7OH (C16E7) and water by using simultaneous measurements of shear stress/small-angle light scattering (Rheo-SALS) and shear stress/small-angle X-ray scattering (Rheo-SAXS) [2]. The lamellar-to-onion transition with decreasing temperature has been reported for a C10E3 and C12E4 systems, which is explained in terms of decrease in the saddle-splay modulus of bilayers with decreasing temperature [3]. Our findings are apparently controversial with these results. However, we have recently found a system which exhibits both types of transition, i.e., the lamellar-to-onion-to-lamellar transition with increasing or decreasing temperature. We have also found that the onion phase forms a closed loop in a temperature-concentration diagram at a constant shear rate. The results are discussed in terms of the saddle splay modulus of bilayers and the effective surface tension at rest. The transition mechanism is also discussed based on the rheo-SAXS experiments around the lower and upper transition temperatures.

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IN SITU LARGE AMPLITUDE OSCILLATORY SHEAR (LAOS) EXPERIMENTS ON ROD-LIKE VIRUSES AND COLLOIDAL PLATELETS

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Highly anisotropic particles are by nature susceptible to external fields. In particular shear forces can cause a pronounced shear thinning, where a highly viscous unordered system is sheared into a low viscous ordered system. This makes shear thinning behavior both fundamentally and practically interesting. The rheological and structural responses of the system at the onset of shear thinning can be conveniently studied by large amplitude oscillatory shear (LAOS) in combination with in situ scattering techniques. Here we study two systems: 1) dispersions of rod-like (fd) viruses approaching the isotropic - nematic transition in combination with time-resolved small-angle neutron scattering; 2) dispersions of gibbsite platelets around the nematic phase in combination with time-resolved small-angle X-ray scattering. Viewing the responses as indicating a sequence of physical processes, we identify, for the rod-dispersions, a region of purely elastic response accompanied by an increase in the orientational ordering. By yielding this is followed in sequence by a region of fluid-like behavior at an almost constant ordering. The platelet dispersions display, for a broad range of frequencies, a transition from singlet feature in the scattering at small strain amplitude to a doublet at large strain amplitude. This suggests the existence of a critical strain for reorienting the platelets, which is not reflected in the bulk rheology.

AMPHIPHILIC STRUCTURE AND SOLUBILITY IN IONIC LIQUIDS

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Even the simplest protic ionic liquids, exemplified by ethylammonium nitrate (EAN), exhibit a liquid structure with some of the characteristics of an amphiphilic self-assembly phase. The ensuing nanostructure has profound implications for their miscibility with molecular and other ionic liquids, and for their solvency for simple, complex and macromolecular solutes. Recently we have elucidated several key aspects of the structure of ionic liquids, their mixtures and solutions primarily using small and wide angle neutron scattering and low-resolution diffraction techniques. In this paper we will describe the effects of mixtures of ionic liquids with water, mixtures of two ionic liquids, and of metal salt solutions on the structure of a variety of ammonium-based protic ionic liquids. The behaviour of larger and more complex solutes, including nonionic amphiphiles and poly(ethylene glycol), will also be described.

SELF ASSEMBLY OF CATIONIC SURFACTANTS AND BLOCK COPOLYMERS IN PROTIC IONIC LIQUIDS

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Nanoscale self-assembly in ionic liquids (IL) is of great interest as these fluids have special thermal and chemical stability, negligible vapor pressure, high ionic conductivity and wide electrochemical window. In this work we study self-assembly and the structure-rheological properties relationships of amphiphilic Pluronic block copolymers (triblock copolymers made of a central polypropylene oxide (PO) and two end polyethylene oxide (EO) blocks) dissolved in a protic ionic liquid (ethylammonium nitrate, EAN). Using a combination of experimental methods including rheology, cross-polarized light microscopy, and small angle neutron scattering, we characterized the phase diagram of the Pluronic/IL model system: F127 (EO106PO70EO106)/EAN and L121(EO5PO70EO5)/EAN. The length of the EO block has a significant effect on the shear viscosity and elastic modulus of the micellar aggregates. Spherical micelles are formed for higher Mw EO blocks, which stabilizes the highly curved spherical interface. For lower EO Mw steric effects are less significant and the interface curvature is lowered, forming cylindrical (wormlike) micellar aggregates. Spherical micellar solutions behave as non-birefringent Newtonian liquids whereas wormlike micelles show a considerable viscoelasticity and strong flow birefringence. A comparison with pluronic self-assembly in water is interpreted with molecular thermodynamics, providing guidance for the self-assembly of non-ionic surfactants and block copolymers in ionic liquids. The self-assembly of didodecyldimethylammonium bromide (DDAB) in a protic ionic liquid, ethylammonium nitrate (EAN), in the high concentration regime, is studied using five different experimental techniques. A thermo-reversible first order sponge (L3) to lamellar (La) transition occurring at [DDAB] > 80 wt% was evidenced by (1) a sharp increase in the elastic and viscous moduli, (2) a transition peak recorded by differential scanning calorimetry, (3) formation of Maltese cross birefringence textures observed via polarizing optical microscopy, (4) a decrease in the inter-bilayer mean distance measured by small angle neutron scattering and (5) an abrupt increase in the conductivity obstruction factor. In contrast to aqueous DDAB solutions, this surfactant forms a stable L3 phase in EAN in a wide window of compositions and temperatures, which is potentially useful for the synthesis of nanoporous material. To the best of our knowledge, this is the first evidence of the formation of the L3 phase in an ionic liquid.

LAMBDA-PHAGE DNAs CONFINED BY LIPID MEMBRANES: SOFT STRINGS AGAINST SOFT SURFACES

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It has been recently shown[1] that when a bio-adhesive phospholipid vesicle is brought into contact with a carpeted surface of end-grafted lambda-phage DNAs, the spreading front of the adhesive patch propagates outwards from a nucleation center, acting as a scraper that strongly stretches the DNA chains. Moreover, the multiple bonds created during vesicle spreading effectively staple the stretched chains in the gap between the membrane and the substrate, creating a tunnel-like channel for the DNA chains. The chain configuration starts thus at its fixed, end-grafted point at the streptavidin substrate, a protein layer of the receptors conjugate to the ligand biotin that end-functionalizes the short polymers to some of the bilayer phospholipids. From its grafted end, the chain meanders through the forest of short polymer bonds that connect the phospholipid membrane above the chain to the protein bed below it, eventually exiting the adhesive gap to adopt a coil-like configuration in the corner between the vertical vesicle wall and the protein surface. Such an experimental geometry provides an unique tool for studying single DNA stretching and confinement in a biomimetic environment[2,3]. In this contribution we analyze the conformations of single and double end-grafted DNA chains in the neighborhood of the, almost vertical, phospholipids walls at the border of the adhesive patch. Average images of the fluorescence emitted by these chains allow for a direct visualization of the segment distribution of polymer chain conformations in restricted geometries. The observed distributions can be quantitatively compared to the predictions from polymer theory for monomer concentrations of chains grafted by one or two ends onto a flat surface or at a corner at the intersection of two flat surfaces. [1] - Hissette M.L., Haddad P., Gisler T., Marques C.M., Schröder A.P., *Soft Matter*, 4, 828 (2008). [2] - Nam, G., Hissette, M.L., Sun, Y. L., Gisler, T., Johner, A., Thalmann, F.; Schröder, A.P., Marques, C.M., Lee, N.K. *Phys. Rev. Lett.*, 105, 088101 (2010). [3] - Thalmann, F.; Billot, V.; Marques, C.M. *Phys. Rev. E*, 83, 061922 (2011).

PHYSICAL CHEMISTRY OF VIRAL EVOLUTION

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Physical virology presents a new direction that aims to provide a physical-chemical description of common mechanisms controlling viral replication for a broad range of viruses. The viral genome is enclosed in a rigid single-molecule-thick protein shell ("capsid"). In many situations the highly negatively charged genome is hundreds of times longer than a capsid's dimension. This physical genome confinement leads to high pressure on the capsid. We address basic conceptual facts that lead to high pressure in the viral capsid, and hence to the virus being infectious. Pressurized double-stranded DNA viruses provide a unique physical system to study the physical chemistry of strongly confined DNA. Since all viral capsids are permeable to water and ions, viral genome interactions are modulated by the chemical potential of water molecules hydrating the DNA. At DNA-DNA separations between 10 and 30Å, the electrostatic forces are dominated by the hydration force. With micro-calorimetry (Isothermal Titration Calorimetry) and atomic force microscopy (AFM) a systematic investigation of the role of DNA hydration force on viral genome ejection and packaging was conducted. We found that besides from being responsible for a pressure driven DNA release from a virus, water hydrating the genome inside the capsid is also exerting a supporting osmotic pressure on the interior of the capsid walls. Thus, the hydration force provides mechanical capsid stabilization against external deformation. In order to investigate the effects of the external cellular environment on DNA hydration inside and outside the capsid, packaged DNA length, temperature, salt and osmotic pressure have been varied.

Safekeeping of viral genetic material, successful delivery of the genome into the host cell, and survival between infections when viruses are susceptible to a variety of mechanical damage, defines the concept of viral metastability. We argue that the DNA hydration force is responsible for a balance between all of these factors, which are critical to the virion. Since the hydration force is directly dependent on the DNA packaging density, there is an intimate coupling between the physical-chemical evolution of the virus' dimensions and the genetic evolution of viruses. Insight into the physical-chemical aspect of viral evolution is provided.

MOLECULAR ASSEMBLY TO PROTOCELL

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Synthesizing simple living cells that contain the minimal elements necessary to perform the basic functions of life will provide insight into the biophysical origins of life. Development of the model vesicle system having the self-reproducing and the membrane traffic abilities is the first step for autopoietic cycles. In the present cell systems, such membrane deformations are managed by complex interplays between membrane proteins and lipids. It is hypothesized that one role of the membrane proteins is to introduce a local spontaneous curvature by interacting with the membranes, although the relationship between the local spontaneous curvature and the shape deformations has not been demonstrated. In this context, we have introduced the local spontaneous curvature in the membrane by coupling spontaneous curvatures of lipids with a phase separation. The binary giant unilamellar vesicle (GUV) composed of the inverse-cone-shaped lipids and cylinder-shaped lipids showed vesicle adhesion through the domains rich in inverse-cone-shaped lipids by forming an hourglass-like interbilayer structure called a stalk. On the other hand, in the binary vesicle composed of cone- and cylinder-shaped lipids, the main chain transition of cone-shaped lipids reduces the surface area, which results in the pore formation. Furthermore by using lipids with a phosphoethanolamine head group (PE-lipids) we demonstrated a model self-reproducing vesicle system, where the vesicles continuously formed new generation vesicles with identical composition by the temperature cycling. These model vesicle systems shed light on the physical aspects of the development of the protocell.

Posters

**Association in Solution III
*Self-Assembly: From Bio-Colloids to Nano-
Engineering***

Bifröst University, Iceland

July 23-27, 2012



Engineering Conferences International

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25. *Molecular Interaction and Microstructure of Cationic Polyelectrolyte-Anionic Surfactant Complex Systems: Effect of Polyelectrolyte Charge Density and Surfactant Alkyl Chain Hydrophobicity.*
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FABRICATION OF SILICA COATED MAGNETIC NANOPARTICLES

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Magnetic properties of nanoparticles enable these nanoscale structures to be oriented and self-assembled when a magnetic field is applied. In these structures dipole-dipole interactions between adjacent magnetic particles couple them together and force the reversible formation of anisotropic structures. The self-assembly of nano-particles into higher organizations in a controlled manner has critical. The behaviour of Fe_3O_4 magnetic nanoparticles (MNPs) with an average size of 6 nm under the enhanced magnetic force has been studied on various template surfaces. However, Fe_3O_4 nanoparticles (magnetites) have hydrophobic surfaces. To be able to use MNPs in bio-applications, their surface properties have to be made hydrophilic.

In order to make the surfaces hydrophilic, two coating methods have been employed: a) in situ synthesis of silica coated magnetic nanoparticles where both magnetite synthesis and the coating occur in the same reaction mixture and magnetites are synthesized via coprecipitation method, and b) coating of the pre-prepared magnetites. In both methods the reaction takes place in aqueous core of water-in-oil (w/o) microemulsions to dominate dispersibility and stability, since reverse micelles are isotropic, thermodynamically stable, single-phase systems. AOT is the surfactant used in all microemulsions, where n-heptane is the continuous oil phase.

CRYSTALLINE NANOPARTICLE DISPERSIONS DO NOT RIPEN

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We have studied the ripening in crystalline and amorphous nanoparticles dispersions, using time resolved light scattering methods. While amorphous particles undergo classical Ostwald ripening, governed by an interfacial tension and the monomer solubility and diffusion coefficient, the crystalline dispersions do not. Rather, their size distributions remain essentially stationary in time. Data from three different compounds are presented and the molecular origin of the observations is discussed.

INTERMEDIATE RANGE ORDER IN PROTEINS AND COLLOIDAL SUSPENSIONS

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The colloidal cluster phase is an equilibrium thermodynamic state characterized by the reversible aggregation of colloidal particles to a finite, energetically favored size. Clusters can arise from a competition between a short range attraction, driving aggregation, and a long range repulsion, which stabilizes the clusters to a finite size. These structures may produce unique properties and are also known precursors to gelation and arrested states. We have developed an efficient method of modeling ground state cluster structures, validated by previous basin-hopping Monte Carlo (MC) simulations, indicating a preferred close packed spherical structure, regardless of the form of short range attraction. However, at finite temperature entropy and Brownian motion cause deviations from ground state expectations, resulting in the unique phase behavior observed experimentally.

Scattering experiments and liquid state theory on such systems sometimes show a low- q peak in their structure factor, indicating a length scale of strong particle correlation. Using metropolis MC simulations, the structure factor is decomposed into the contributions from correlations between monomers and particles in a cluster, two particles in clusters, and two monomers. In a clustered state, the low- q peak is determined mainly by correlations between particles in clusters. Monomer dominated and percolated systems also produce a low- q peak, but one that depends on all three types of correlations. Consequently, we conclude that the low- q peak represents intermediate range order (IRO) rather than cluster formation explicitly. Further, particle correlations and cluster size distributions indicate distinct mechanisms of percolation between states within and outside of the two phase region. These simulations provide guidelines to predict the conditions of cluster formation in protein and colloidal solutions. Cluster solutions can then be engineered to produce unique structures and properties for applications in the biopharmaceutical and nanotechnology industries.

LIPID SEGREGATION ABOVE T_m : THE CASE AGAINST HOLEY VESICLES

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Binary mixtures of long and short chain phospholipids (e.g. DMPC and DHPC) have been extensively used as model membrane systems. They have been used with NMR to probe protein structures and have even been employed in membrane protein crystallization. More recently their effects on human skin have been studied, where they have been shown to increase the elasticity and permeability without irritating the stratum corneum. They have also shown the potential to enhance or even retard drug absorption during percutaneous drug delivery.

At low temperatures, well below the transition temperature, T_m , for the long chain lipids, discotic micelles, or bicelles, have unambiguously been shown to form. At higher temperatures appropriate to most applications, the situation is less clear, though it is mostly now understood that discotic micelles do not survive above T_m . At sufficiently high temperatures, far above T_m , most work suggests some kind of lamellar phase exists. For a very specific range of mixtures at those temperatures, extremely monodisperse, unilamellar vesicles have been shown to spontaneously form and are thought to hold huge promise for drug encapsulation and gene therapy. Several studies have suggested that the lamellae in these high temperature phases contain perforations, pore-like curvature defects whose edges are lined with DHPC molecules. Understanding if and when (and even how to control) such pores might form will clearly have major implications on their efficacy as delivery vehicles.

Recently Yamada and co-workers claim to have confirmed the formation of such DHPC rimmed nanopores in DMPC/DHPC vesicles using fluorimetry to monitor the leakage (and subsequent quenching) of a fluorescent dye. While nanopores would clearly lead to such leakage, we suggest that other mechanisms could provide defects through which the dye could leak and segregation at such high temperatures seems unlikely. In order to verify our hypothesis we performed small angle neutron scattering measurements using deuterated long chain DMPC contrast matched to the solvent in order to locate the short chain DHPC molecules within the vesicle. Our measurements confirm that the DHPC is fairly uniformly distributed throughout the vesicle rather than concentrated around pores therein.

INSIGHTS INTO MEMBRANE THICKNESS FLUCTUATIONS

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Biological membranes are supramolecular aggregates that harbor many chemical reactions essential to cellular function. They are self-assembled highly flexible structures that have the ability to undergo an array of dynamic conformational transitions which are vital to many biological processes. These motions range from individual lipid oscillation, to the undulation of large (micron size) patches of the membrane. At atomic to molecular length scales the diffusion of individual lipids within the membrane have been shown to affect cell signal transduction while at the large length scales membrane stiffness and fluidity have been shown to have a significant impact on cellular uptake and release. The dynamics at intermediate length scales are fundamental to understanding how the large scale motions emerge from atomic and molecular movements and interactions, yet remain experimentally elusive. At this intermediate length scale thickness fluctuations have been suggested theoretically and even proposed as a mechanism for membrane pore formation. The insertion and functioning of membrane proteins is believed to be heavily influenced by such dynamics. While such fluctuations have never been experimentally observed in lipid membranes, some computational work has been undertaken to evaluate the characteristic features of such fluctuations with simulation snapshots clearly showing thickness fluctuations on the order of several Angstroms.

We have utilized neutron spin echo spectroscopy, complemented by small angle neutron scattering, to experimentally verify these fluctuations in a pure, fully saturated, phosphocholine unilamellar vesicle (ULV) lipid bilayer system. In order to specifically highlight the thickness fluctuations we utilize tail deuterated lipids. These fluctuations appear as an excess in the dynamics of undulation fluctuations. Like the bending rigidity, the thickness fluctuations change dramatically as the lipid transition temperature, T_m , is crossed, appearing to be completely suppressed below the transition. Above the transition the relaxation rate is on the order of 100 ns and is independent of temperature. The amplitude of the thickness fluctuations is $3.7 \text{ \AA} \pm 0.7 \text{ \AA}$, which agrees well with theoretical calculations and molecular dynamics simulations. The dependence of the fluctuations on lipid tail lengths is also investigated and determined to be minimal in the range of 14 to 18 carbon tails. Insertion of pore forming proteins in the membrane seem to both increase the rigidity and decrease the thickness fluctuations in the membranes, similar to the effect of lowering the temperature below T_m .

SELF-REPRODUCTION OF LIPID VESICLES

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Evolution of molecular assemblies toward a cellular life is fascinating research field in soft matter science. So far extensive investigations have been performed to construct a protocell, origin of the cellular life, using well-defined organic molecules. Especially modeling of a self-reproduction vesicular system is a key concept to understand origin of the cellular life.

In typical self-reproduction vesicle systems, membrane precursors are converted into membrane molecules with the help of a catalyst. These membrane molecules are incorporated into the vesicle, and the vesicle show self-reproduction. There are two pathways in this self-reproduction system, the birthing and the budding. In the birthing pathway, new synthesized membrane molecules form daughter vesicles inside a mother vesicle. When the daughter vesicle grows to a certain size, it extrude through the membrane of the mother vesicle to the environment. On the other hand, in the budding pathway, the mother vesicle deforms to pear-like shape and is divided into two independent vesicles. We established a model self-reproduction vesicle system without the membrane molecule synthesis route. The model vesicle composed of cylinder- and inverse-cone-shaped lipids formed inclusion vesicles inside the mother vesicle, and the inclusion vesicle was expelled by a temperature cycling. By changing the vesicle composition, the mother vesicle deformed to pear-like shape and is divided into two independent vesicles. A key concept of this system is the coupling of the main- chain transition and the shape of lipids.

A THEORETICAL APPROACH TO PHASE COEXISTENCE IN TERNARY CHOLESTEROL-PHOSPHOLIPID MIXTURES

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We first introduce a simple and predictive model for describing the phase stability of ternary Cholesterol-phospholipid mixtures. Assuming that competition between the liquid and the gel phase of the phospholipids is the main driving force behind lipid segregation, we derive a phenomenological Gibbs free-energy of mixing, based on the calorimetric properties of the lipids main transition. Gibbs phase diagrams are numerically obtained that reproduce the most important experimental features of DPPC-DOPC-Chol membranes and of other ternary mixtures. Regions of triple coexistence and liquid ordered-liquid disordered segregation as well as the temperature behavior of this diagram are well described by our model. We also developing a Ginzburg-Landau description of spatial heterogeneities seeking a quantitative explanation for the outer domains line tension and for phenomena such as microscope domains nucleation. J.Wolff, C.M. Marques, F. Thalmann, PRL,106,128104 (2011)

NANO-EMULSIFICATION THROUGH SURFACTANT HYDRATION: THE PIT AND PIC METHODS REVISITED

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Bottom-up routes are now accepted as the most efficient way to produce nano-materials. However, both design and control of the systems and processes remain an important challenge. Indeed the wide-spread conception that these methods involve pathways far from equilibrium makes it difficult to link the macroscopic behavior with the microscopic structures.

Outstanding examples of these short-comings are the emulsification methods that involve rapid changes of the surfactant layer amphiphilicity, through hydration of the surfactant head. The Phase Inversion Temperature (PIT) and Phase Inversion Composition (PIC) methods are already wide-spread in the industry but further developments require to understand precisely their mechanisms. The main claim is that a fine emulsification takes place through phase inversion because of low-interfacial tensions in its vicinity.

We have investigated these methods with both model and technical systems and radically challenge this claim. We demonstrate that the non-equilibrium pathways are closely linked to the equilibrium phase behaviors and microstructures through particular states we observe at a given composition line : the Clearing Boundary. These states are not related to phase inversion and we show that phase inversion is not required to achieve nano-emulsification. We control the emulsification outcome solely by controlling the microstructure of the CB state. For example in the sub-PIT method the CB state is a superswollen microemulsion produced under gentle shear and subsequently quenched through cooling, whereas in the sup-PIC method the CN state is a bicontinuous sponge phase which decomposes into small oil droplets upon dilution. Therefore the nano-emulsions are produced through self-assembly of the ternary water/surfactant/oil systems followed by a quench to gain metastability.

Our conclusions open a systemic way to design triggers and systems for a given nano-emulsification outcome and gather general knowledge on such useful methods.

CONTROLLED EMULSION DROPLET SOLVENT EVAPORATION FOR THE CONTINUOUS AND CONSISTENT PRODUCTION OF PARTICLES

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In this work, we are interested in the production of particles of uniform size and shape, with no variation in morphology or chemical heterogeneity, using the emulsion droplet solvent evaporation method. This method is extremely versatile, and can be applied to a range of materials, for example, to create magnetic nanoparticles, polymeric Janus beads, and crystalline particles. The emulsion droplets act as confined spaces, or templates, within which the particles can form. Upon removal of the solvent, primary magnetite nanoparticles pack into dense magnetic clusters, polymers precipitate as beads, or small molecules crystallize out of the solution to form spherical particulates.

We introduce the use of membrane emulsification and pervaporation as operations that have the potential to be integrated into a continuous and high-throughput production process for such particles. We show that membrane emulsification offers precise control of the droplet sizes, which is important in such applications as designing nanoparticles to act as building blocks for new materials, or crystallizing active ingredients for pharmaceuticals. Furthermore, pervaporation is an efficient method of removing the solvent from the emulsion and allows for the controlled evaporation of multiple solvents by changing the sweep gas on the outside of the pervaporation fibers.

We developed a population balance model to describe the transport of solvent from nanocrystal- or polymer-laden oil droplets in an O/W emulsion as it flows through a pervaporation unit. The solvent transport was simulated using a high-resolution finite volume algorithm, which provided a smooth solution with second-order accuracy. The dominant resistance was in the aqueous phase and the solubility of the solvent in water was found to have a significant effect on the solvent transport rate. In addition, the evolution of the particle size distribution as it shifted to smaller sizes was found to be the most gradual for small amounts of solvents with low water solubility due to broader concentration gradients in the aqueous phase. This model offers insight into how solvent is removed from emulsion oil droplets as they flow down a pervaporation fiber and may be useful as a design tool.

NANO-FOAMS BY 'CONTINUITY-INVERSION' OF DISPERSIONS (NF-CID)

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Our new approach utilizes the nanodisperse gaps in dense amorphous or crystalline packings of colloidal polymer lattices. Polymer particles with a size between 20 and 500 nm were produced by emulsion polymerization of styrene and methylenemethacrylate. The nanodisperse gaps were filled with supercritical fluids CO₂ and N₂, respectively, at appropriate pressures and at temperatures below but close to the glass transitions of the respective polymer. As the glass transition was traversed a 'continuity inversion' was observed, the formerly discrete polymer particles becoming a continuous polymeric material with nanodisperse inclusions of the supercritical fluid. A subsequent expansion led to a foaming process with a fixation of the polymer foam as temperature and/or pressure dropped. Optimization of the reaction conditions led to foams with pore sizes smaller than 1 µm. We will discuss the nature of the foams and how the choice of the polymer in combination with the choice of the supercritical fluid affects the pore size and density of the resulting foams.

FLOW INSTABILITY AND SHEAR BANDING IN A MULTI LAMELLAR VESICLE SYSTEM

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Complex fluids may be affected by the flow field due to interrelation between flow and structure, yielding many different structures and structural transitions in lamellar phases under shear flow. Here, we have studied multi lamellar vesicle (MLV) formation in a nonionic lamellar phase under continuous shear flow. Spectacular viscosity oscillations were observed at shear rate of 2 s^{-1} together with a shear banded flow. These phenomena are uncommon in lamellar phase (L_α) systems. Using rheology and rheo-Small Angle Neutron Scattering (SANS) we were able to relate the shear bands to the viscosity behavior. Moreover we correlated the viscosity oscillations to the MLV fraction. We found that the viscosity oscillations are well described by a sinusoidal wave of period c.a. 19 minutes. The obtained rheology results are discussed in connection to the observed shear-induced structure changes.

NUCLEAR MAGNETIC RESONANCE AND RHEOLOGY INVESTIGATION OF CRYSTALLIZATION PHENOMENA IN VEGETABLE OILS

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Lipids come in two forms, liquid and solid fats. The solid fats are relevant from the industrial point of view for several reasons. For instance they can give the desired texture to the final foods and are suitable for the existing process conditions. On the other hand they can cause cardio-vascular diseases or increase cholesterol levels etc. Organogel liquid oils are possible replacers, rich in unsaturated fats and therefore less dangerous for human health. Here we present a structural investigation of organogels, based on olive oil, cocoa butter and commercial monoglycerides of fatty acids (Myverol), by using rheological methods (i.e. small amplitude oscillations) and Nuclear Magnetic Resonance (NMR), aiming at evidencing the crystallization phenomena and the change in material structure due to formulation and operating conditions. In particular we used the NMR technique to estimate the spin spin relaxation time (T_2) distributions by applying the Inverse Laplace Transform to the echo-decay obtained by the Carr-Purcell pulse sequence. The NMR methodology gave a deeper understanding on the organogel structure confirming the results obtained through the rheological characterization. In fact the structural analysis evidenced, depending on the observed temperature range, the presence of different polymorph structures that caused relevant changes in rheological parameters during the temperature ramp tests.

RHEO-NMR OBSERVATIONS OF COMPLEX FLUIDS

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Homogeneous flow becomes unstable in many complex fluids above a certain strain rate. The system may be separating into two bands of differing viscosity with the higher strain rate band being typically more ordered. Shear banded flow has been seen in systems as diverse as self-assembled surfactant structures, emulsions, semi-dilute polymer solutions, colloidal suspensions and soft glasses. More recently, time fluctuations of this banding structure have become of interest, as seen in recent publications by both theorists and experimentalists [1].

Experiments were carried out using Rheo-NMR velocimetry methods, that allow to non-invasively image the velocity field of the fluid with a time resolution ranging from milliseconds to seconds. Our challenge is to develop pulse sequences which allow both dimensionality and speed. The former being important as theoretical work suggests fluctuations in vorticity direction, which implies the requirement of a full 3D velocimetry for experiments. While difficult for competitor techniques involving light or ultrasound scattering, 3D capability is natural to NMR.

We aim on presenting current methods and results for canonical wormlike micelle systems, for example, CPyCl/NaSal in brine. Strain-controlled cylindrical Couette cells are used with approximately 1 mm gap size inside a 25 mm outer cylinder that fits into a 400 MHz wide-bore Bruker NMR system. The focus will be on the time dependence of the band structure and the nature of inherent spatio-temporal fluctuations.

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TUNING MICROSTRUCTURE OF NON-IONIC MICELLAR NETWORKS: RHEOLOGY AND SELF-DIFFUSION INVESTIGATIONS

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Through a combination of rheology and NMR-PGSE techniques we were able to monitor the structural transition from branched to disconnected micellar network formed by the PhosphatidylCholine (PC), a well known phospholipid commonly extracted by natural sources (soybean). PC can be dissolved in a large variety of organic solvents, giving rise in many cases to the formation of reverse water-in-oil wormlike micelles in presence of trace amounts of water. Previous investigations showed that PC reverse micelles can undergo either to a sphere-to-rod-to-sphere transition if the dispersing organic phase is cyclohexane (cC6) or to the formation of a multiconnected network of cylindrical micelles if the oil is isooctane (iC8). From the point of view of phase equilibria, in cC6 a Winsor II-type phase separation is observed above a threshold value of the water/PC molar ratio (W_0) whereas a phase separation between a dense gel and almost pure oil (gas-liquid) is found above a critical W_0 value in iC8. Although the scenario is expected to be far more complex when these two types of hydrocarbons that individually form different topological defects are mixed, the use as a solvent of cC6/iC8 solutions could allow a fine tuning of the branch density. In the present work we intend to investigate the influence of the composition of cC6/iC8 mixture, described through the isooctane weight fraction $R = \text{wt}(cC6)/[\text{wt}(cC6)+\text{wt}(iC8)]$, on the microstructure and how this can be coupled to the other control parameter defined by W_0 . The results are discussed in terms of relative capacity of both the mixed solvents (R -control parameter) and water (W_0 -control parameter) to swell the paraffinic PC chains and head group size, respectively, those parameters making energetically favourable end-caps, branch junction points, or a combination of both.

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DEFORMATION HARDENING AND FORMATION OF SHEAR BANDS UNDER FRICTION OF COPPER AT DIFFERENT LUBRICANT CONDITIONS

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Friction and wear of copper rubbed with lubrication in wide range of loads and sliding velocities were studied. The results of friction and wear experiments are presented as the Stribeck curve where the boundary lubrication (BL), mixed and elasto-hydrodynamic lubrication (EHL) regions are considered. The structural state of subsurface layers in different lubricant regions was studied by different spectroscopic and microscopic techniques. Dislocation density as well as nanohardness at thin surface layers in EHL and BL regimes was determined and compared.

The dominant friction and wear mechanisms in different lubrications regions are discussed. Severe plastic deformation (SPD) of subsurface layers under friction is correlated with nanocrystalline structure obtained by different methods of grain refinement. It was found that SPD of thin surface layers under friction is accompanied by formation of shear bands in sublayers of contact spots. The main difference between the friction conditions is different gradients of strain, hardness and temperature.

A MICROFLUIDIC PLATFORM FOR SMALL-ANGLE X-RAY SCATTERING: FROM NEMATIC ALIGNMENT AT THE LIQUID CRYSTAL-WATER INTERFACE TO NEUROFILAMENT SELF-ASSEMBLY

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Microfluidics involve precise control and manipulation of fluids under sub-millimeter confinement. The technology opens new exciting research and technological possibilities, such as lab-on-a-chip applications, diagnostics and particle synthesis, among others.

From a small-angle scattering and association in solution point of view, the advantages of using such a platform are also enormous. In first place, the manipulation of fluids allows for an experimental control (e.g. rate of mixing, shear rate, concentration gradients, confinement) that has been previously unavailable, opening the possibility for new experiments. In second place, sample consumption is reduced to the microliter scale, allowing experiments with expensive and rare materials. In third place, the constant flow of material prevents radiation damage (critical for X-ray synchrotron radiation).

The main projects at our laboratory involve the self-assembly of lipids, nucleic acids and cytoskeletal proteins and we are currently developing a microfluidic device to perform experiments on such soft materials. As a proof of concept of the new platform, we were able to study the alignment of the nematic phase of 5CB (4-Cyano-4'-pentylbiphenyl) at the interface with water under flow. A jet of nematic liquid crystal is flown through the middle of a 100 μm wide channel, surrounded by a water-triton X-100 (2 wt%) solution. As we scan along the nematic jet, we observe that the nematic director orientation changes when the X-ray beam goes from the nematic-water boundary (where the nematic director is tilted relatively to flow) to the middle of the jet (the director is parallel to flow). We interpret this change in orientation to be caused by the discontinuity of the velocity gradient at the boundary between both liquids. To the best of our knowledge, this is the first time that the orientation of nematic liquid crystals at the interface with water is studied under flow, and this result is of relevance both on a fundamental level of understanding of liquid crystalline flow and for practical applications (e.g. boundary lubrication).

Currently, our efforts are centered on the study of the self-assembly process of neurofilaments, with emphasis on bundle formation.

CHEMICAL PROCESSING BY SWARM ROBOTICS

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Chemical robots are in principle artificial cells, with the exception of the ability to evolve and self-replicate. The main components of such a synthetic cell are (i) a "body" (shell) that defines properties such as size, shape, hardness and should facilitate the exchange of molecules with the environment similarly as a cell membrane, (ii) the internal space with compartments which should process absorbed molecules and release or accumulate products of chemical reactions. Chemical robots should also have the ability to move either passively or actively in the surrounding medium, and to adhere to target substrates or objects. Chemical robots may be used for targeted drug delivery, recovery of valuable chemicals from dilute resources, environmental clean-up, as smart diagnostic devices, or other applications.

Most of goals of the bottom-up fabrication of chemical robots satisfying the ideas described above are covered by research activities of Chemical Robotics Laboratory in the Institute of Chemical Technology Prague. The research team of the laboratory already has great experience with the synthesis of various types of particles serving as chemical robots' bodies (hollow silica particles, liposomes, thermo-responsive hydrogel particles, core-shell alginate and chitosan particles), synthesis of internal compartments and their loading with the desired content (chemical payload), encapsulation of the mixture of internal compartments into an outer shell and functionalization of the outer shell (chemical robot's body) surface. The functional properties of individual chemical robots such as controlled molecular transport or structural changes in response to surrounding changes are also studied. Furthermore there is a continual need of precise study of chemical robot movement and collective behavior.

The functionality and applicability of chemical robots in general depends strongly on both the inner functionality of individual robots (molecular exchange, chemical processing) and the external abilities to behave as living cells. The aim of present work is to study such external properties, namely it will focus on these two problems: a) the oriented movement in a given environment (artificial chemotaxis), and b) coordination of their actions in swarms, collective behaviour and the adhesion to targets and one other robots (reversible aggregation).

TOWARDS UNDERSTANDING PEPTIDE SELF-ASSEMBLY: A MODEL SYSTEM STUDY

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The trifluoroacetate (tfa) salt of the synthetic peptides (ala)_nlys, with n = 4, 6, 8, 10, have been investigated in order to understand the effects of hydrophobic interactions on peptide self-assembly. The peptides carry a net positive charge that ensures colloidal stability of the self-assembly structures through a long-range electrostatic repulsion. It has been found that a difference of 2 amino acids in the sequence leads to drastic changes in the self-assembly structures. A4K does not form any aggregates in the aqueous solutions of volume fraction, ϕ , $\phi = 0.41$. A6K self-assembles in water into very long, hollow nanotubes with radius $R = 26$ nm, above a critical aggregation concentration $\phi_{cac} = 0.10$. The monolayer-wall nanotubes, as indicated by SAXS data, reach close packing already at $\phi = 0.15$ and upon further increasing the concentration, a novel phase transition to lamellar phase where the peptide molecules form bilayers consisting of two, presumably oppositely oriented monolayers, occurs. For A8K and A10K, the self-assembly structure is fibrils with a finite size of circa 200 nm and a rectangular cross section of 4x8 nm as deduced from SAXS measurements.

LAMELLAR GEL NETWORKS BASED ON ANIONIC SURFACTANTS AND FATTY ALCOHOLS: STUDY OF STRUCTURE IN HAIR COLORANTS

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Through the collaboration between the Procter and Gamble Company and the University of Strasbourg, we are carrying out research of gel network structures based on anionic surfactants and fatty alcohols.

These systems are defined as 3-dimensional networks of planar bilayer sheets of lipids in aqueous solutions. Depending on the hydrocarbon chains packing and water content, the lamellae can be in a $L\beta$ phase, which is a rigid gel phase formed below the lipids main transition temperature. This organization of lamellae can retain a large amount of water, drives thickening of formulations and offers powerful structuring and stabilizing properties.

Gel network technology is used as water-based delivery chassis for pharmaceuticals and beauty care products such as skin care creams, hair conditioners and hair colorants. From technology development point of view it is of importance to understand the structure and the compositional boundaries of gel networks in order to achieve stable and efficacious products.

This oral presentation focuses on the understanding of the homogeneity, spatial organization and structure of the bilayers in a lamellar gel network based on alkyl phosphate surfactants. Mechanism of instability of such gel network as a function of the ionic strength and fraction of lipids is proposed.

The results from various methods including small angle X-ray scattering, electron and light microscopy, fluorescence techniques, ultracentrifugation, light scattering and rheology will be presented to demonstrate structural correlations.

PHASE BEHAVIOR AND SELF-ASSEMBLY IN THE LECITHIN/SQUALANE SYSTEM

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The phase behavior and self-assembly in the lecithin/squalane system were investigated by means of small angle x-ray scattering, NMR self-diffusion and polarized light microscopy. The phase diagram show a large isotropic liquid phase with a miscibility gap (liquid-liquid phase separation) at lower lecithin concentrations, with a critical temperature of ca. 90 °C. The isotropic phase is very viscous and lecithin has a low diffusion coefficient indicating that lecithin is aggregated into reverse worm like micelles as has been reported with other alkanes. At higher lecithin concentrations a complex liquid crystalline phase behavior is observed.

STRUCTURE AND DYNAMICS OF MICROEMULSION NETWORKS LINKED BY END-CAPPED STAR POLYMERS OF VARIING FUNCTIONALITY

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Microemulsions are, in general, isotropic, thermodynamically stable, and low viscous liquids in which mixtures of oil and water are stabilized by the presence of surfactant. However, for a variety of situation the technical applicability of microemulsions is limited by their low viscosity. Therefore the control of viscosity of microemulsions is a highly interesting and important topic. One logical option is to cross-link the O/W droplets by bridging amphiphilic polymers, a concept which works well with endcapped PEO, where the interconnection of droplets leads to a substantial increase in viscosity once passing an effective percolation concentration of droplets and polymer. Our interest now was to study multiply endcapped polymers, i.e. star-like amphiphilic, as a function of the degree of functionality for multiple connections, thereby interrelating the molecular architecture of the amphiphilic copolymer to its effect on the rheological properties. Accordingly we have investigated various multiply bridging polymers and their effect on the structure and dynamics of water in oil microemulsion droplets. For that purpose we synthesized such bridging amphiphilic polymers with multiple linkers by the RAFT procedure, allowing to control the number of arms (functionality), the length of the hydrophilic group (maximum length for connection) and of the hydrophobic chain (stickiness). In our experiments we employed various molecular architectures of end-capped star polymer. A detailed structural picture was obtained by SANS measurements, especially with respect to the effects on the droplet sizes and even more on the interactions in the microemulsion systems. In addition, dynamic light scattering and rheology measurements going to high frequencies were carried out. The results of our experiments show a systematic effect of the polymer length, the number of arms and the length of the stickers on the structure and therefore the physical properties of the microemulsion networks created by the presence of the multi-bridging polymers.

TUNABLE COMPLEX FLUIDS BY CYCLODEXTRIN INCLUSION COMPLEXATION

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The existence of tunable interactions in polymer solutions gives the ability to control the microstructure and rheological properties. For example, hydrophobically modified water soluble polymers (HMP) are widely used as rheology modifiers in paints, cosmetics, pharmaceuticals, foods, enhanced oil recovery, water treatment and controlled release of bioactive materials. Tuning the strength of interactions can change phase behavior from soluble, low viscosity solutions, to gels, to precipitates. Theories of the structure and dynamics of association fluids rely on binary interactions. However, hydrophobic interactions always result in clustered hydrophobic domains. Similar to hydrophobic association, the inclusion or host-guest interaction between cyclodextrins and hydrophobic groups is another reversible physical interaction which can be used to modulate polymer solutions. The internal cavity of CD is hydrophobic and can accommodate suitable hydrophobic groups driven by a non-covalent interaction to form inclusion complex. If CDs are grafted in polymer chains, novel polymer networks can be generated by this kind of host-guest interactions between polymers with hydrophobe and CD side-groups. In contrast to purely hydrophobically modified polymer association the complexes have a distinct binary stoichiometry, an unusual temperature dependence, and a resistance to solvent polarity changes. The rules for assembly of cyclodextrin-based complex fluids will be discussed. In contrast to purely hydrophobically modified polymer association the complexes have a distinct stoichiometry, an unusual temperature dependence, and a resistance to solvent polarity changes.

NON-TRADITIONAL BLOCK COPOLYMER DIRECTED KINETIC SELF-ASSEMBLY

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We have developed a block-copolymer-directed, kinetically-controlled self-assembly process called Flash NanoPrecipitation (FNP) to produce 50-400 nm nanoparticles. The process involves controlling micromixing to effect supersaturations as high as 10,000 in 1.5 ms, and then controlling nucleation and growth rates to match block copolymer assembly rates. The initial focus was on highly insoluble compounds where high supersaturation was easily achieved. Our recent interest has been on compounds that are less hydrophobic and ways to achieve high supersaturation and rapid, controlled precipitation. We will present approaches that use specific interactions to drive precipitation. Examples include electrostatic complexes between lipids and siRNA to create therapeutic nanoparticles; acid/base interactions between weak base drugs and acidic salts, and coordination chemistry. Finally, the use of purely electrostatic repulsions to create a range of nanoparticles from pure polymers, without additives enables new fundamental studies of polymer glass transitions under nanometer confinement.

COMPUTER SIMULATIONS OF A THERMO-RESPONSIVE POLYMER IN AQUEOUS SOLUTION

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Poly-(N-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer that possesses a lower critical solution temperature (LCST) in the physiological temperature range at 305 K. We have performed Molecular Dynamics simulations with an OPLS force field for single and multiple ($n=1$, $n=10$) PNIPAM chain solutions in water. Large fluctuations of the physical properties of the single chain make it difficult to clearly identify a possible LCST. However, we do observe indeed a sudden drop in size and volume of the $n=10$ system at 305 K, which is absent for the $n=1$ system at the same concentration. Using the Amber force field we have studied the behavior of the polymer under the influence of planar and cylindrical (graphene-like) walls. Furthermore, we have investigated the feasibility of a thermodynamic machine that harnesses the conformation changes of the polymer for mechanical contractions and expansions.

MOLECULAR INTERACTION AND MICROSTRUCTURE OF CATIONIC POLYELECTROLYTE-ANIONIC SURFACTANT COMPLEX SYSTEMS: EFFECT OF POLYELECTROLYTE CHARGE DENSITY AND SURFACTANT ALKYL CHAIN HYDROPHOBICITY

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Adsorption of anionic surfactants onto cationic polyelectrolytes can result in associative phase separation over a broad range of mixture compositions, with the gel-like concentrated phase (coacervate) rich in both polymer and surfactant. There is a substantial literature of applied research on formulating coacervates for successful applications in food, consumer health care products, and pharmaceutical industries. Of particular interest is the delivery and controlled release of active compounds (i.e., functional oil, antibacterial agent) via coacervation during the usage of many consumer health care products. The successful design of an appropriate coacervation and delivery process best incorporates knowledge of the molecular interactions governing such self-assembling systems. Such interactions govern the coacervate microstructures and physical properties (i.e. adhesion and rheology). Consequently, a deeper understanding of the molecular interaction-structure-property relationship in coacervation systems is of significant fundamental scientific interest. We have investigated a systematic variation of model mixtures, to assess the significance of polymer charge density and surfactant alkyl chain hydrophobicity, holding as many of the auxiliary properties constant. This allows of providing a quantitative molecular-level interpretation of these effects and linking this to the desired phase behavior, microstructure and coacervate rheological performance. We have combined a wide range of experimental measurements, ranging from thermodynamic measurements (Isothermal Titration Calorimetry (ITC)), to microstructure characterization techniques (Small-Angle Neutron Scattering (SANS), Small-Angle X-ray Scattering (SAXS), Dynamic Light Scattering (DLS), cryo-Transmission Electron Microscopy (cryo-TEM)), and rheology at different structural levels (Bulk rheology and Nano-indentation atomic force microscopy (AFM)). All those techniques provide extensive evidence of the molecular interactions. The phase behavior study resolves the characteristic coacervation-redissolution phase transitions. Modeling of the molecular interaction using a statistic thermodynamic theory of adsorption and polymer-bound, free micelles calculation enables a semi-empirical quantification of the polyelectrolyte/surfactant association behavior. The molecular-level interactions are shown to be governed by both electrostatic and hydrophobic interactions, with relative importance depending on the polymer's charge density and surfactant's tail hydrophobicity. Coacervation is tied to charge equivalence at low surfactant concentrations, while resolubilization is shown to be related to the colloidal stability of surfactant-polyelectrolyte complexes. Finally, increasing polymer charge density leads to dramatic changes in terms of coacervate microstructure, which also corresponds to the increased shear and elastic coacervate moduli.

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Engineering Conferences International

Engineering Conferences International (ECI) is a not-for-profit global engineering conferences program that has served the engineering/scientific community since 1962 as successor program to Engineering Foundation Conferences. ECI has received recognition as a 501(c)3 organization by the U.S. Internal Revenue Service and is incorporated in the State of New York as a not-for-profit corporation.

The program has been developed and is overseen by volunteers both on the international Board of Directors and international Conferences Committee. More than 1,400 conferences have taken place to date. The conferences program is administered by a professional staff and the conferences are designed to be self-supporting.

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To serve the engineering/scientific community with international, interdisciplinary, leading edge engineering research conferences

ECI Purposes

The advancement of engineering arts and sciences by providing a forum for the discussion of advances in the field of science and engineering for the good of mankind by identification and administration of international interdisciplinary conferences

To work with engineering, scientific and social science societies and the interested general public to jointly sponsor conferences and to take other actions that will foster complementary programming.

To initiate conferences that will have a significant impact on engineering education, research practice and/or development.

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Ideally, proposals should be submitted from 18 to 24 months in advance of the conference although the staff can work on a shorter timeline.

The traditional format for an ECI conference is registration Sunday afternoon with technical sessions held each morning and evening through Thursday or Friday noon. Afternoons are used for informal gatherings, poster sessions, field trips, subgroup meetings and relaxation. This format has served well to build important professional networks in many areas.

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- Publicize via electronic and print media.
- Administer all finances including grants, contributions and purchase orders. (ECI makes grant funds available as soon as a grant is approved.) There is no need for chairs to set up a conference bank account or file tax returns for their conference.
- Process all applications and registrations.
- Produce bound program/abstracts book.
- Contract for the publication of print or electronic proceedings, if any.
- Provide on-site staff during the conference.

For more information, please contact the ECI Director at Barbara@engconfintl.org



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2012

- July 23-27 **12AS ASSOCIATION IN SOLUTION III: SELF-ASSEMBLY-FROM BIO-COLLOIDS TO NANO-ENGINEERING** (Iceland)
U. Olsson, Lund University; N. Wagner, University of Delaware
- July 30-Aug 3 **12AE BIOLOGICAL AND PHARMACEUTICAL COMPLEX FLUIDS: NEW TRENDS IN CHARACTERIZING
MICROSTRUCTURE, INTERACTIONS AND PROPERTIES** (Tomar, Portugal)
S. Amin, Malvern Instruments Limited; M. Solomon, Univ. of Michigan
- August 12-17 **12AR RARE EARTH MINERALS/METALS – SUSTAINABLE TECHNOLOGIES FOR THE FUTURE** (San Diego, CA)
D. Tao, Univ. of Kentucky; R. Honaker, Univ. of Kentucky; S. Chuanyao, BRGRIMM; K. Delaney, Rare Earth Industry
and Technology Association; B. Hiskey, Univ. of Arizona; R. Darolia, GE Aviation (retired)
- Sept 23-28 **12-AN NONSTOICHIOMETRIC COMPOUNDS V** (Sicily, Italy)
J. Janek, Justus-Liebig Univ. Giessen; L. Malavasi, Univ. of Pavia; T. Kawada, Tohoku Univ; R. O'Hayre, Colorado
School of Mines
- Sept 24-26 **12AO FIFTY YEARS OF WATERSHED MODELING – PAST, PRESENT AND FUTURE** (Boulder, CO)
A.S. Donigian, AQUA TERRA Consultants; Richard Field, US EPA
- Sept 30-Oct 5 **12AQ HARNESSING MATERIALS GENOME: ACCELERATED MATERIALS DEVELOPMENT VIA COMPUTATIONAL
AND EXPERIMENTAL TOOLS** (Vail, Colorado)
J.-C. Zhao, The Ohio State Univ.; M. Asta, Univ. of California Berkeley; Peter Gumbsch
Institutsleiter Fraunhofer-Institut fuer Werkstoffmechanik IWM; B. Huang, Central South University
- Oct 7-11 **12AF OLIGONUCLEOTIDE DELIVERY: BIOLOGY, ENGINEERING AND DEVELOPMENT** (Hernstein, Austria)
L. Sepp-Lorenzino, Merck & Co., Inc.; S. F. Dowdy, Univ of California San Diego School of Medicine
- Oct 7-12 **12-AV FIBROUS NANOCOMPOSITES** (Crete, Greece)
P. Gouma, SUNY at Stony Brook; A. Mitraki, Univ. of Crete; S. Zhang, MIT
- Oct 14-19 **12AM ADVANCED MEMBRANE TECHNOLOGY V** (Singapore)
T. Fane, Nanyang Technological Univ.; R. Wang, Nanyang Technological Univ.
- Oct 21-25 **12AG MODELING, SIMULATION, AND OPTIMIZATION FOR THE 21st CENTURY ELECTRIC POWER GRID**
(Lake Geneva, Wisconsin)
M. Petri, Argonne National Laboratory; P. Myrda, Electric Power Research Institute

2013

- Jan 6-11 **13AG FUNCTIONAL GLASSES: PROPERTIES AND APPLICATIONS FOR ENERGY AND INFORMATION** (Sicily, Italy)
H. Jain, Lehigh Univ.; C. Pantano, The Pennsylvania State Univ.; S. Ito, Tokyo Institute of Technology; K. Bange,
Schott Glass (ret.); D. Morse, Corning.
- Jan 21-23 **13AT CELL-BASED THERAPIES II** (San Diego, CA)
C. Mason, Univ. College London; G. Russotti, Celgene; L. Nielsen, AIBN
- March TBA **12AX OVERCOMING THE TECHNICAL AND ENVIRONMENTAL CHALLENGES OF HYDRAULIC FRACTURING
FOR SHALE GAS** (TBA)
D. Reible, Univ. of Texas; M. Macdonell, Argonne National Laboratory
- Spring TBA **13AJ FUNCTIONAL DIELECTRIC MATERIALS FOR POWER ELECTRONICS, ENERGY STORAGE AND ENERGY
HARVESTING** (Kyoto, Japan)
M. Lanagan and C. Randall, The Pennsylvania State University; T. Tsurumi, Tokyo Institute of Technology;
N. Murayama, AIST

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Spring TBA	13AK	MASSIVE ENERGY STORAGE FOR THE BROADER USE OF SUSTAINABLE AND RENEWABLE ENERGY SOURCES (Vancouver, Canada) S. Neti, Lehigh University; T. V. Nguyen, University of Kansas
May 25-30	13AF	FLUIDIZATION XIV: FROM FUNDAMENTALS TO PRODUCTS (Noordwijkerhout, The Netherlands) J.A.M. Kuipers and N.G. Deen, TU Eindhoven; R.F. Mudde and J.R. van Ommen, Delft Univ. of Technology)
May 13-17	13AS	BEYOND NICKEL-BASED SUPERALLOYS (Bad Berneck, Germany) U. Glatzel, Univ. of Bayreuth; B. Bewlay, General Electric Global Research; L. Cornish, Univ. of Witwatersrand; M. Heilmaier, Univ. of Darmstadt; J. Schneibel, (formerly) Oak Ridge National Laboratory; D. Shifler, Office of Naval Research; H. Stone, Rolls-Royce Univ. Technology Centre, Cambridge; K. Yoshimi, Tohoku Univ.
June 2-5	13AO	ADVANCES IN OPTICS FOR BIOTECHNOLOGY, MEDICINE AND SURGERY XIII (Lake Tahoe, California) J.W. Tunnell, Univ. of Texas at Austin; M. Fitzmaurice, Case Western Univ.; A.C. Boccara, ESPCI-Paris Tech
June 16-20	13AM	BIOCHEMICAL AND MOLECULAR ENGINEERING XVIII (Beijing, China) Honorary Chairs: Daniel I.C. Wang, MIT; Pinkai Ouyang, Nanjing Chemical University H. Zhao, Univ. of Illinois; D. Robinson, Merck;
July TBD	13AV	INTERNATIONAL SYMPOSIUM ON ENVIRONMENTAL DAMAGE UNDER STATIC AND CYCLIC LOADS IN STRUCTURAL MATERIALS AT AMBIENT TEMPERATURES (Bergamo, Italy) A.K. Vasudevan, Office of Naval Research; H. Holroyd, Luxfer, Inc.; R. Ricker, NIST; N. Moody, Sandia National Laboratories
Summer TBA	13AI	LIGHT-ACTIVATED TISSUE REPAIR: MECHANISM, OPTICAL PARAMETERS AND THERAPEUTIC APPLICATIONS (Brazil TBA) J. Anders
Summer TBA	13AC	MATERIALS CHALLENGES IN SOLAR ENERGY (Tomar, Portugal) V. Renugopalakrishnan, Northeastern University; P. Somasundaran, Columbia University; D. Miller, Argonne National Laboratory; C. Chinnasamy, Electron Energy Corporation; Nazario Martin Leon, Univ. Madrid; Emilio Palomares, Institute of Chemical Research of Catalonia; Luis Maesal, Universitat Rovira I Virgili
Sept TBD	13AD	FROM PURE TO DOPED CARBON-BASED NANOMATERIALS: RECENT ADVANCES AND APPLICATIONS (Spain) R. Arenal, Univ. of Zaragoza; C.P. Ewels, Univ. de Nantes; D. Goldberg, NIMS and Univ. of Tsukuba; V. Meunier, Rensselaer Polytechnic Institute; M. Motta, Thomas Swan & Co., Ltd.; R. Rubio, Max Planck Inst.
Oct TBD	13AE	ENZYME ENGINEERING XXII (Toyama, Japan) Y. Asano, Toyama Prefectural Univ.; L. Giver, Codexis
Oct TBD	13AH	VACCINE DELIVERY AND STABILIZATION (Eastern US) Robert Evans, Merck; Mark Kendal, University of Queensland
Oct 6-11	13AN	NANO- AND MICROMECHANICAL TESTING IN MATERIALS RESEARCH AND DEVELOPMENT IV (Portugal) J. Michler, EMPA
Nov 3-7	13AL	COMPOSITES AT LAKE LOUISE 2013 (Lake Louise, Alberta, Canada) V. Thompson, New York University; J. Lewis, University of Illinois
<u>2014</u>		
March-April TBD	14AG	GEOPOLYMERS (Europe TBD) C. Leonelli, Univ. of Modena and Reggio Emilia; W. Kriven, Univ. of Illinois at Urbana-Champaign; mA. R. Boccaccini, Univ. of Erlangen-Nuremberg
April TBD	14AC	CELL CULTURE ENGINEERING IV (Eastern Canada) A. Kamen, National Research Center Canada; Weichang Zhou, Genzyme
June TBD	14AA	VACCINE TECHNOLOGY V (Mexico TBD) L. Palomares, UNAM; M. Cox, Protein Sciences Corp.; J. Aunins, Janis Biologicals; K. Jansen, Wyeth Vaccine Research
June 3-8	14AY	METABOLIC ENGINEERING IX (Vancouver, Canada)
June 17-22	14AP	POROUS MEDIA AND ITS APPLICATIONS IN SCIENCE, ENGINEERING AND INDUSTRY V (Kauai or Kona, Hawaii) K. Vafai, Univ. of California, Riverside