



11th WORKSHOP
Fribourg 04.06.2013

Pérolles II, building G, room G230
Boulevard de Pérolles 90, Fribourg

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Local Organizers

Véronique Trappe
Andreas Zumbühl
Frank Scheffold

Program

10.00-10.20	Registration / Coffee	
10.20-10.25	<i>Welcome: Véronique Trappe (U Fribourg)</i>	
<i>Chair: Marco Lattuada (U Fribourg)</i>		
10.25-11.10	Jan Vermant (University of Leuven) Interfacial rheology: instrumentation and applications to particle laden interfaces.	
<i>Interfaces and Confined Environments</i>		
11.10-11.30	Isa (ETHZ)	Adsorption energies of poly(ethylene oxide) based surfactants and nanoparticles on an air-water interface
11.30-11.50	Ecoffet (CNRS Mulhouse)	Characterizing surface properties with photonic force microscopy
11.50-12.10	Araújo (ETHZ)	Adsorption of functionalized colloids on substrates
12.10-12.30		Introduction to posters
12.30-14.00	Lunch/Coffee/Posters/Discussion	
<i>Chair: Paolo De Los Rios (EPFL)</i>		
14.00-14.20	Nelson (ETHZ)	Studying complex nanoparticle self-assembly at liquid interfaces using pendant drop tensiometry, micro-rheology and fluorescence correlation spectroscopy
14.20-14.40	Farahpour (U Sharif)	Chain deformation in translocation phenomena
14.40-15.00	Vobornik (EPFL)	Study of DNA polymorphisms using high-resolution frequency modulation AFM based strategies
<i>Bulk Rheology</i>		
15.00-15.20	Farage (U Fribourg)	Ab initio normal stress coefficients and viscosity for colloidal dispersions
15.20-16.00	Coffee/Posters/Discussion	
<i>Chair: Kitty van Gruijthuijsen (Firmenich)</i>		
16.00-16.20	Mütze (ETHZ)	Systematic analysis of shear bands in wormlike micelle solutions
<i>Materials</i>		
16.20-16.40	Sander (ETHZ)	Functional colloidosomes for controlled transport and release made by microfluidic and bulk emulsification
16.40-17.00	Simon (U Fribourg)	Functional iron oxide nanoparticles as reversible cross-links for magnetically addressable shape-memory polymers
17.00-17.20	Zabara (ETHZ)	Perforated bicontinuous cubic phases with pH-responsive topological channel interconnectivity
17.20	<i>Closing Remarks: Justyna Czerwinska (U Bern)</i>	

Poster Contributions

1	Wüest (U Bern)	Water flow in highly confined carbon channel
2	Reinhardt (U Fribourg)	Depletion forces, the structural precursor to freezing and geometrically driven self-assembly in 2D
3	Colombo (ETHZ)	Microscopic picture of cooperative processes in restructuring gel networks
4	Japaridze (EPFL)	Monitoring conformational changes of proteins by AFM
5	Vebert (U Geneva)	DNA hybrids structure formation
6	Toughraï (U Basel)	Functional surfaces through biomimetic block copolymer membranes
7	Niebel (ETHZ)	Multifunctional alumina microplatelets for tailoring interfacial bonding in bio-inspired composites
8	Müller (U Fribourg)	Synthesis and characterization of artificial phospholipids
9	Calzolari (U Fribourg)	Cononsolvency of PNiPAM at the transition between solvation mechanisms

Posters in support of talks

	Mütze (ETHZ)	Systematic analysis of shear bands in wormlike micelle solutions
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Abstracts Talks

Adsorption energies of poly(ethylene oxide) based surfactants and nanoparticles on an air-water surface

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The self-assembly of polymer-based surfactants and nanoparticles on fluid-fluid interfaces is a process central to many applications including dispersion stabilization, creation of novel 2D materials and surface patterning (1). Very often these processes entail the compression of interfacial particle or polymer monolayers to obtain the desired material microstructure; at high surface pressures, soluble objects may desorb from the interface and therefore a direct way of measuring adsorption energies becomes of high interest. Moreover, a geometric description linking adsorption energy and wetting properties through the definition of a contact angle can be established for rigid nano or microparticles, but such description breaks down for deformable or aggregating objects. I will present some recent data where we used a novel microtensiometer tool (2) in combination with traditional surface pressure measurements to measure directly the desorption of various types of PEO-based polymers and nanoparticles. Our data show a linear scaling between molecular weight and adsorption energy for PEO chains whose values depend on the sub-phase composition. Moreover, for PEO-stabilized nanoparticles, the desorption surface pressure corresponds to the saturation surface pressure for spontaneously adsorbed monolayers and corresponds to trapping energies of $\sim 10^3$ kT. The values of the surface concentration at desorption confirm particle deformation, as observed using x-ray microstructural characterization. (3)

(1) Boker, A., J. He, T. Emrick, and T.P. Russell. "Self-assembly of nanoparticles at interfaces." *Soft Matter* 3 (2007): 1231–1248.

(2) Zell, Z.A., S.Q. Choi, L.G. Leal, and T.M. Squires. "Microfabricated deflection tensiometers for insoluble surfactants." *Applied Physics Letters* 97 (2010): 133505.

(3) Isa, L., et al. "Core-shell nanoparticle monolayers at planar liquid-liquid interfaces: effects of polymer architecture on the interface microstructure." *Soft Matter* 9 (2013): 3789–3797.

Characterizing surface properties with photonic force microscopy

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While optical tweezers are currently and widely used for micromanipulation studies, their application to fluidic and rheology studies still remains underexplored. However, the tracking of the Brownian motion of particles that are optically trapped is particularly

insightful. For instance, information on their diffusivity can be deduced. These experiences and measurements are of particular relevance when performed in a confined geometry, interfacial forces and phenomena, and therefore the stability of colloids and emulsions being highly sensitive to such confinement (fluidic channels, flow past structured and functionalized walls). The applications of this new optical tool are thus very large, although the quantitative evaluation (relevance of measured quantities), the limits of the method and the potential artifacts need to be further assessed.

The aim of our work is to develop the use of an optical tweezers device as a standard tool for the study of surface properties. In this communication, studies of the brownian motion of a micronic particle approaching surfaces with different hydrophilicity will be presented. Relationships between diffusivity of the particles and macroscopic surface properties will be established.

Adsorption of functionalized colloids on substrates

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Colloids with functionalized surfaces yield directionality of interactions being ideal building blocks for the rational development of self-assembled structures with novel physical properties. Studies of their equilibrium phase diagrams have revealed a myriad of possibilities as, for example, the capability of fine tuning the density and the temperature of the gas-liquid and sol-gel transitions. However, the kinetics of self-organization and the feasibility of assembling the predicted structures are still poorly understood. In order to shed light on the aggregation of patchy colloids we have studied numerically their irreversible adsorption on substrates and analyzed the structure of the resulting colloidal networks.

For the adsorption of three-patch colloids, the network density profile exhibits three distinct structural regimes: surface layer, liquid film, and interfacial region (1); each one with interesting scaling properties. For a mixture of three- and two-patch colloids, we found a non-monotonic dependence of the density on the fraction of two-patch colloids. This result contrasts with the equilibrium counterpart where the density of the film strictly decreases.

We also considered the adsorption of $2A_nB$, with two types of patches (A and B) and dissimilar AA , AB , and BB binding probabilities. Two different growth regimes and a depletion zone close to the substrate are found depending on the binding probabilities and the number n of B patches (2).

(1) C. S. Dias, N. A. M. Araújo, M. M. Telo da Gama, Phys. Rev. E 87, 032308 (2013).

(2) C. S. Dias, N. A. M. Araújo, M. M. Telo da Gama, Soft Matter (2013). DOI: 10.1039/c3sm50386k.

Studying complex nanoparticle self-assembly at liquid interfaces using pendant drop tensiometry, micro-rheology and fluorescence correlation spectroscopy

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Trapping at the interface, combined with lateral mobility and the presence of specific interactions, makes self-assembly of colloidal particles at liquid-liquid interfaces (SALI) a process with huge potential for the creation of controlled structures, including novel ultrathin membranes and capsules.

It has recently been demonstrated in our group that superparamagnetic iron oxide nanoparticles (NPs) stabilized by low molecular weight poly(ethylene glycol) (PEG) shells (1,2), can be self-assembled into saturated monolayers at the water/n-decane interface (3,4). Understanding the basics of SALI is a keystone in turning these NP assemblies into composite membranes suitable for applications. In particular, measuring the viscoelastic properties of the interfacial assemblies in situ and on the micro-scale is of paramount importance (5).

Particle characterisation using pendant drop tensiometry (PDT) has been completed at different concentrations to compare the effects of different PEG shells on the interfacial adsorption behaviour of the particles. Particles with longer linear PEG chains show the highest surface activity and the fastest adsorption kinetics. Master curves have been created for the different particle types, demonstrating the concentration dependence of adsorption speed.

To further investigate the behaviour of the nanoparticles at the decane-water interface, the mechanical properties have been characterised via the tracking of probe particles with very different sizes. Micron-sized tracer particles observed with fluorescence optical microscopy still show diffusive behaviour at the interface upon adsorption of the NPs. Fluorescence correlation spectroscopy, using quantum dots as tracers (6), was used to investigate the interface on the same length scale as the NPs. Surprisingly, these tracers also showed purely diffusive behaviour, with a progressive slowing down ascribed to NP adsorption. It was thus possible to follow the build-up of the NP monolayer with time, and to obtain master curves for the diffusion coefficient as a function of a concentration-dependent effective time, similar to the PDT master curves.

(1) E. Amstad, T. Gillich, I. Bilecka, M. Textor, and E. Reimhult. 2009. *Nano Letters* 9:4042–4048.

(2) T. Gillich, C. Acikgo, L. Isa, A. D. Schlueter, N. D. Spencer, and M. Textor. 2013. *ACS Nano* 7:316–329.

(3) L. Isa, E. Amstad, M. Textor, and E. Reimhult. 2010. *Chimia* 64:145–149.

(4) L. Isa, E. Amstad, K. Schwenke, E. Del Gado, P. Ilg, M. Kroeger and E. Reimhult. 2011. *Soft Matter* 7:7663–7675.

(5) F. Ortega, H. Ritacco, R. G. Rubio. 2010. *Current Opinion in Colloid & Interface Science* 15:237–245.

(6) D. Wang, S. Yordanov, H. M. Paroor, A. Mukhopadhyay, C. Y. Li, H. Butt, and K. Koynov. 2011. *Small* 7:3502–3507.

Chain deformation in translocation phenomena

Farnoush Farahpour [1], Fathollah Varnik[2], Mohammad Reza Ejtehadi[1]

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[2] ICAMS, Ruhr-Universität Bochum, Germany

Deformation of single stranded DNA in a translocation process before reaching the pore is investigated. By solving the Laplace equation in a suitable coordinate system and with appropriate boundary conditions, an approximate solution for the electric field inside and outside a narrow pore is obtained. With an analysis based on the "electrohydrodynamic equivalence" we determine the possibility of the extension of a charged polymer due to the presence of an electric field gradient in the vicinity of the pore entrance. With a multi-scale hybrid simulation (LB-MD), it is shown that an effective deformation before reaching the pore occurs, which facilitates the process of finding the entrance for the end monomers. We also highlight the role of long range hydrodynamic interactions via comparison of the LB-MD results with those obtained using a Langevin thermostat instead of the LB solver.

(1) Greg C Randall and Patrick S Doyle. *Macromolecules*, 38(6):2410–2418, 2005.

(2) Meni Wanunu, Will Morrison, Yitzhak Rabin, Alexander Y Grosberg, and Amit Meller. *Nature Nanotechnology*, 5(2):160–165, 2010.

(3) Stefan W Kowalczyk, Alexander Y Grosberg, Yitzhak Rabin, and Cees Dekker. *Nanotechnology*, 22(31):315101, 2011.

Study of DNA polymorphisms using high-resolution frequency modulation AFM based strategies

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It is an often ignored fact that DNA is a polymorphic molecule having at least a dozen of stable conformations observed in diffraction measurements (1). Depending on the environmental conditions and on the nucleobase sequence, DNA can switch from one conformation to another. This can cause dramatic differences in the overall shape and size of the molecule, and consequently in the physical properties and nanotechnology applications of DNA in nano-templating and DNA nanoelectronics (2). Specifically, when placed in UHV, DNA gets dehydrated and is supposed to change its conformation from B-form to A-form DNA (1). However, this change was never observed after DNA has been deposited on a solid substrate, and cannot be quantified on the level of single molecules with diffraction techniques. Using several frequency modulation AFM-based strategies we successfully visualized grooves and measured the properties of the DNA helix once it's placed in UHV conditions. Our results show that DNA mostly remains in B-form, but locally parts of DNA change their conformation (3, 4). We also saw an effect of different DNA deposition methods on the ability of DNA to change its conformation (5), and developed a model to quantitatively evaluate the height of small single molecules for non-contact AFM imaging (6). Our data could have important consequences for nanoelectronics and nano-templating DNA applications.

(1) A. Ghosh and M. Bansal, A glossary of DNA structures from A to Z, *Acta Crystallographica D* 59, 620 (2003)

- (2) A. V. Pinheiro, D. R. Han, W. M. Shih, H. Yan, "Challenges and opportunities for structural DNA nanotechnology", *Nat. Nanotechnol.* 6, 763 (2011)
- (3) A. Cerreta, D. Vobornik, G. Di Santo, S. Tobenas, L. Alonso-Sarduy, J. Adamcik, G. Dietler, "FM-AFM constant height imaging and force curves: high resolution study of DNA-tip interactions", *J. Mol. Recognit.* 25, 486 (2012)
- (4) A. Cerreta, D. Vobornik, G. Dietler, "Fine DNA Structure Revealed by Constant Height Frequency Modulation AFM Imaging", in press, *Eur. Polym. J.* (2013)
- (5) A. Cerreta, D. Vobornik, G. Dietler, "Comparison of Deposition Methods for AFM Experiments on DNA", submitted for publication
- (6) D. Vobornik, A. Cerreta, A. Mikhaylov, F. Brasili, G. Dietler, "Quantitative AFM Height Evaluation", submitted for publication

Ab initio normal stress coefficients and viscosity for colloidal dispersions

Thomas Farage, Johannes Reinhardt, and Joseph Brader

Department of Physics, University of Fribourg

In this presentation we calculate from first principles the zero shear rate limit of the shear viscosity and the normal stress coefficients of a colloidal dispersion. Besides recovering the well-known expression for the viscosity, we propose new tractable expressions for the first and second normal stress differences. Although restricted to the zero shear rate regime, the presented formulæ are valid for any volume fraction below the glass transition and any kind of interaction potential. Taking advantage of these developments, we consider a system of colloidal particles interacting through a hard-core attractive Yukawa (HCAY) potential and explore the interplay between the attraction strength and the volume fraction. We show that the corresponding curves of our quantities of interest exhibit nontrivial features when close to the critical point and when close to the reentrance into the glassy state.

Systematic analysis of shear bands in wormlike micelle solutions

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[2] Laboratory of Neutron Scattering, PSI, Villigen

Within appropriate physical and chemical conditions, such as temperature, surfactant concentration and pH, surfactant molecules can self-assemble into long and flexible chains, which are called wormlike micelles. Aqueous solutions of such aggregates show a viscoelastic flow behavior: the rheological response can be divided into a model-like linear flow and a complex non-linear flow (1). Subsequently, a wide variety of complex structures are formed with the applied shear-flow. The formation of shear induced structures (SIS) and shear-banding is unique for each solution and only visible in non-linear flow conditions caused by the breakage, recombination and alignment of the micelles. In more detail, below a critical shear stress τ_c (in the Newtonian and shear thinning regime) a minor flow alignment of the micelles is observed and the solution appears transparent. Above τ_c a strong alignment (isotropic to nematic phase-transition) results in the formation of alternating transparent and turbid shear bands along the Couette axis (Fig. 1a) (2).

To capture the structural properties of the shear bands, time-resolved SANS measurements coupled with the rheological data acquisition are performed (Fig. 1b). To map out of the formation and morphology of the shear bands, we analyze them at different shear stresses, temperatures, concentrations, and D_2O/H_2O ratios.

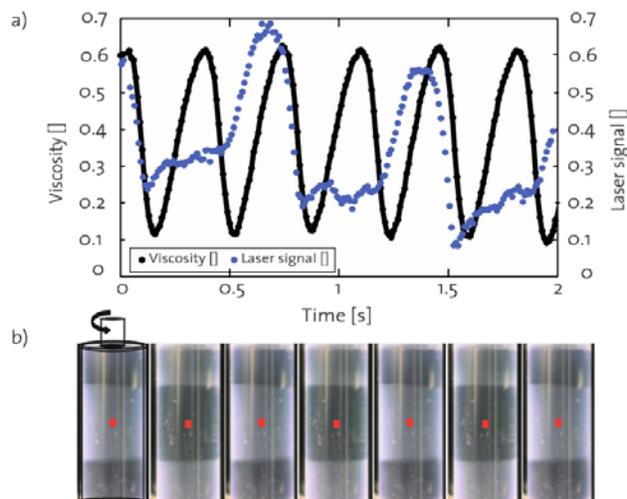


Figure 1: a) Viscosity and laser-light signal as function of time; b) Corresponding visual appearance of shear bands (the laser position is indicated as squares)

- (1) V. Herle et al., Phys. Rev. Lett. 2007, 99, 158302.
- (2) V. Herle et al., Euro. Phys. J. E, 2008, 26, 3.

Functional colloidosomes for controlled transport and release made by microfluidic and bulk emulsification

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Encapsulation and release from microcapsules are of great interest for many applications. Capsules exhibiting nanoparticle shells, known as colloidosomes, are particularly interesting due to their tunable permeability and size. Colloidosomes assembled from double emulsion templates can be made with multiple particle layers in the wall and are thus more robust against defects and have a controllable thickness. In this work, we show how such thick-walled colloidosomes can be assembled and functionalized for guided transport and triggered release by adding active particles into the shell and inside the capsules. Double emulsion templates are made in glass capillary microfluidic devices or using bulk emulsification techniques. Using interfacial rheology and single particle contact angle measurements we show that surface active molecules and surface active particles form an interfacial film at the oil-water interface which is crucial for the effective stabilization of the double emulsion templates (1). With this approach, we make colloidosomes from many materials such as silica, $Al_2O_3-Fe_3O_4$ or tricalcium phosphate/clay mixtures that can for instance be transported using external magnetic fields (2). The addition of cargo-loaded particles inside such capsules opens several possibilities for the controlled release of cargo with well-defined spatial temporal patterns, including onetime release, switchable on-off release or co-release of different substances (3). The use of specially modified particles that form a strong viscoelastic film on the inner water droplet enables the application of bulk techniques for double emulsification. Since bulk techniques usually lead to polydisperse emulsion droplets we cannot reach the high efficiency and precise control over droplet dimension that is

possible with microfluidic emulsification. However, the proposed bulk emulsification approach opens the possibility for high-throughput colloidosome production and for assembly of colloidosomes in a size range much smaller than previously realized (4). The good control over the transport and release from colloidosomes and the ability to produce them small and in large quantities make them attractive for many fields and applications.

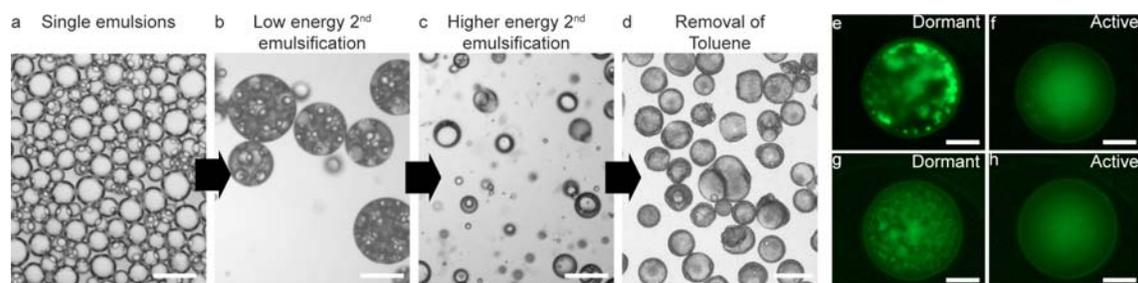


Figure 1: Bulk double emulsification in two steps: a) single emulsions; b,c) double emulsions after b) low and c) higher energy shearing. d) Colloidosomes after removal of toluene (scale bars 100 μm). e-h) Sequential switchable release of a fluorescent dye from colloidosomes made by microfluidic emulsification. e, g) Dormant state: dye is encapsulated; f, h) active state: dye is released (Scale bars 50 μm).

- (1) J.S. Sander, L. Isa, P.A. Rühls, P. Fischer and A.R. Studart: Stabilization mechanism of double emulsions made by microfluidics, *Soft Matter*, 2012, 8, 11471
- (2) J.S. Sander and A.R. Studart: Monodisperse functional colloidosomes with tailored nanoparticle shells, *Langmuir*, 2011, 27, 3301–3307
- (3) J.S. Sander and A.R. Studart, Particle-filled complex colloidosomes for tunable cargo release submitted, 2013
- (4) J.S. Sander and A.R. Studart, Functional multiwalled colloidosomes made small and in large quantities via bulk emulsification, in submission, 2013

Functional iron oxide nanoparticles as reversible cross-links for magnetically addressable shape-memory polymers

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 Adolphe Merkle Institute / University of Fribourg

Shape-memory nanocomposites comprising superparamagnetic iron oxide nanoparticles serving both as inductive heating elements and cross-links of a polymeric network will be discussed. Superparamagnetic iron oxide nanoparticles (SPIONs) covered with polymerizable norbornene groups were first fabricated in a one-step co-precipitation method via the oxidation of $\text{Fe}(\text{acac})_3$ in the presence of 5-norbornene-2-carboxylic acid ligands. Weight fractions of SPIONs ranging from 0.1 and 20% w/w were subsequently copolymerized with norbornene via ring-opening metathesis polymerization (ROMP) using a ruthenium alkylidene catalyst (Grubbs' first generation). A sequence of cross-linked polynorbornenes, where SPIONs were very well dispersed, were produced. The incorporation of said particles led to the appearance of a rubbery plateau, and the materials exhibited magnetically-addressable shape-memory behavior, even at low Fe_3O_4 nanoparticle loadings (below 1% w/w). The non-covalent binding of the norbornene ligands covering the surface of the SPIONs enabled melt-processing of these materials at elevated temperature. The shape memory properties were only retained for samples with a high Fe_3O_4 content.

Perforated bicontinuous cubic phases with pH-responsive topological channel interconnectivity

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Lipidic lyotropic liquid crystals are at the frontline of current research for release of target therapeutic molecules due to their unique structural complexity and the possibility of engineering stimuli-triggered release of both hydrophilic and hydrophobic molecules. One of the most suitable lipidic mesophases for the encapsulation and delivery of drugs is the reversed double diamond bicontinuous cubic phase, in which two distinct and parallel networks of ~4 nm-large water channels percolate independently through the lipid bilayers, following a Pn3m space group symmetry. In the unperturbed Pn3m structure, the two sets of channels act as autonomous and non-communicating three-dimensional transport pathways.

Here, we introduce a novel type of bicontinuous cubic phase, where the presence of OmpF membrane proteins at the bilayers provides unique topological interconnectivities among the two distinct sets of water channels, enabling molecular active gating among them.

By a combination of small angle x-ray scattering, release and ion conductivity experiments, we demonstrate that -without altering the Pn3m space group symmetry or the water channels diameter-, the newly designed perforated bicontinuous cubic phase attains transport properties well beyond those of the standard mesophase, allowing faster, sustained release of bioactive target molecules.

By further exploiting the pH-mediated pore-closing response mechanism of the double amino acid half-ring architecture in the membrane protein, we also provide the perforated mesophase with a pH-triggered ON-OFF opening of the pores, enabling a fine modulation of the transport properties by only moderate changes in pH, which could open unexplored opportunities in the targeted delivery of bioactive compounds.

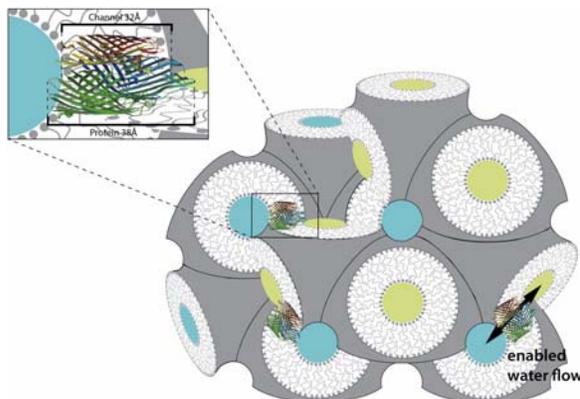


Fig. 1: Schematic representation of the perforated Pn3m cubic phase based on the hybrid lipid monolinolein:OmpF:water system.

(1) A. Zabara, R. Negrini, O. Onaca-Fischer, R. Mezzenga, *Small*, in press (2013).

Abstracts Posters

Water flow in highly confined carbon channel

Simon Wüest, Justyna Czerwinska

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Helium tight graphene oxide membranes showed to selectively pass water vapour (1). The stacked graphene oxide platelets offer highly confined channels which allow water molecules to slip through. This raised the idea of using graphene oxide membranes for novel water purification filters. The performance of such membranes to reject ions and other impurities is the subject of current research (2-3). In order better evaluate graphene oxide membranes as filters; we study the behaviour of water in such confined structures, through molecular dynamics simulations.

We simulated water molecules (TIP3P water model) confined in a 3 nm wide channel and exposed to a constant force. The walls are built of two layers of orthogonally arranged atoms. The two layers are shifted to each other by half an atom-atom distance. Water flow was studied for various forces on three surfaces with increasing atom-atom distance. The walls are assumed to be rigid and the wall atoms are fixed in place. Interaction between the water molecules and the walls are simulated by the Lennard-Jones potentials for water on graphene (4). Simulations were run for thermostated and non-thermostated water.

In such small structures the non-slip boundary condition does not hold and there is slip between the walls and the water (5). The slip length is determined by comparing the effective flow after 0.1 ns simulation time to the expected flow assuming a Poiseuille flow with no slip boundary conditions (5). Non-thermostated simulations, showed a constant slip length for small applied forces. With increasing distance between atoms in the walls, the interaction between the water and the walls increases and leads to a reduced slip lengths. By thermostating the water, slip length is reduced with increasing force because the velocity is constantly truncated.

Slip length strongly depends on the surface structure and is reduced with increasing surface roughness (6). Thermostating the water can lead to non-physical effects (5). Using flexible but thermostated walls could lead to a more realistic model (5).

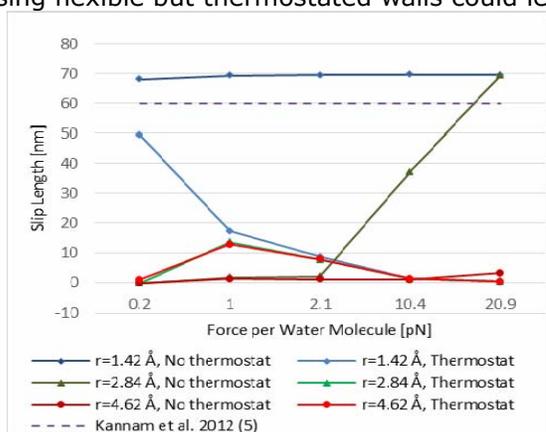


Figure 1: Slip lengths decreases with increasing surface roughness (r is the distance between atoms in the wall). For thermostated simulations the velocity is artificially truncated shows a reduced slip length. For smooth surfaces and all range of forces as well as for rough surfaces and small forces, non-thermostated simulations show a constant slip length.

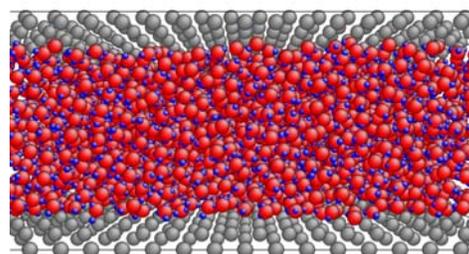


Figure 2: Simulation model: The water molecules are confined between two carbon walls with 3 nm distance. The wall roughness is increased by increasing the atom-atom distance.

- (1) R. R. Nair, H. A. Wu, P. N. Jayaram, I. V. Grigorieva und A. K. Geim, Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes, *Science*, 335(6067), 2012.
- (2) D. Cohen-Tanugi und J. C. Grossman, Water Desalination across Nanoporous Graphene, *Nano Lett.*, 12(7), 2012.
- (3) P. Sun, M. Zhu, K. Wang, M. Zhong, J. Wei, D. Wu, Z. Xu und H. Zhu, Selective Ion Penetration of Graphene Oxide Membranes, *ACS Nano*, 7(1), 2013.
- (4) T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, P. Koumoutsakos, On the Water–Carbon Interaction for Use in Molecular Dynamics Simulations of Graphite and Carbon Nanotubes, *J. Phys. Chem. B*, 107 (6), 2003.
- (5) S. K. Kannam, B. D. Todd, J. S. Hansen, P. J. Davis, Slip length of water on graphene: Limitations of non-equilibrium molecular dynamics simulations, *J. Chem. Phys.*, 136(2), 2012.
- (6) N. V. Priezjev, S. M. Troian, Influence of periodic wall roughness on the slip behaviour at liquid/solid interfaces: molecular-scale simulations versus continuum predictions, *J. Fluid Mech.*, 554, 2006.

Depletion forces, the structural precursor to freezing and geometrically driven self-assembly in 2D

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[1] Department of Physics, University of Fribourg

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Microscopic picture of cooperative processes in restructuring gel networks

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[1] Institute for Building Materials, ETH Zürich

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Colloidal gel networks are disordered elastic solids that can form even in extremely dilute particle suspensions. With interaction strengths comparable to the thermal energy, their stress-bearing network can locally *restructure* via breaking and reforming interparticle bonds. This allows for yielding, self-healing, and adaptive mechanics under deformation. Designing such features requires controlling stress transmission through the complex structure of the gel and this is challenging because the link between local restructuring and overall response of the network is still missing. Here, we use a space resolved analysis of dynamical processes and numerical simulations of a model gel to gain insight into this link. We show that consequences of local bond breaking propagate along the gel network over distances larger than the average mesh size. This provides the missing microscopic explanation for why nonlocal constitutive relations are necessary to rationalize the nontrivial mechanical response of colloidal gels.

- (1) J. Colombo, A. Widmer-Cooper, and E. Del Gado, *Phys. Rev. Lett.* **110**, 198301 (2013)

Monitoring conformational changes of proteins by AFM

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DNA hybrids structure formation

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Relying on the achievement of a general mechanism to eventually solve critical biological and medical issues through the observation and manipulation of biochemical mechanisms, we are investigating the structure formation and modes of interaction of DNA hybrids, in particular copolymer self-assembly and crystallization as well as interpolyelectrolyte complex formation. We are predominantly focusing on reaching a comprehensive understanding of the organization of these peculiar macromolecules which can undergo specific interactions such as biological recognition to ultimately establish a general process of their association.

Functional surfaces through biomimetic block copolymer membranes

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The functionalization of surfaces using biomimetic block copolymer membranes aims at developing smart surfaces for biotechnological applications such as biosensing. Instead of lipid membranes, amphiphilic block copolymer membranes were chosen as mimics of biological membranes due to properties such as tunable thickness, chemical and mechanical stability, lower permeability, fluidity, mobility, etc. Upon insertion of membrane proteins, these systems could allow for the preparation of mechanically and chemically robust and air-stable biosensor devices. ABA-triblock copolymer membranes were successfully prepared and characterized by using two synthesis strategies: the "grafting-from" approach with surface-initiated ATRP from gold supports, and the "grafting-to" approach with Langmuir-Blodgett transfer on germanium supports. Protein insertion experiments were performed by using impedance spectroscopy for gold surfaces and by in-situ ATR-FTIR for germanium surfaces. Results with in-situ ATR-FTIR show the presence of the protein on the polymeric membrane. Polymer brushes such as these, exhibiting a hydrophilic-hydrophobic-hydrophilic sequence, could be regarded as the first example of solid supported, biomimetic block copolymer membranes prepared by a "grafting-from" approach.

Multifunctional alumina microplatelets for tailoring interfacial bonding in bio-inspired composites

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Composite biological materials such as seashells, bone or plant stems are reinforced with fibres or platelets and often achieve an unusual combination of stiffness, strength and toughness. The alignment of the reinforcing elements and the interfacial bonding between them and the continuous polymer matrix are crucial for an effective stress transfer and thus for the reinforcement of the polymer. The surface chemistry of reinforcing particles can be altered to change the interfacial interactions with the matrix, which in turn affects the mechanical response of the composite.(1) Coating the surface of reinforcing microplatelets with superparamagnetic nanoparticles enables their 2D alignment using rotating magnetic fields.(2) Controlling the surface chemistry of reinforcing particles to enable simultaneously deliberate alignment and tunable interfacial bonding in selected polymer matrices is highly desired but has not yet been fully explored. Here, we present a straightforward process to coat alumina microplatelets with a controllable layer of iron oxide nanoparticles, which can be further functionalized with nitrodopamine (ND) to enable deliberate tuning of the platelet surface chemistry.(3) To achieve this coating, alumina platelets and tris(acetyl-acetonato)iron(III) were heated in benzyl alcohol in a nitrogen atmosphere. SEM images show that the platelets are densely covered with nanoparticles that have a size of approximately 10 to 20 nm. XRD measurements confirm the formation of Fe₃O₄. The iron oxide coated platelets show a macroscopic magnetic response, can be aligned in 2D using a rotating magnetic field and have a 10-fold increased ability to adsorb ND compared to the bare platelets. When used as reinforcing particles in an epoxy resin as matrix the amine groups of the ND coating lead to an improved interfacial bonding resulting in an increased flexural strength, flexural modulus and flexural strain at break relative to the composite reinforced with not ND-modified iron oxide coated platelets.

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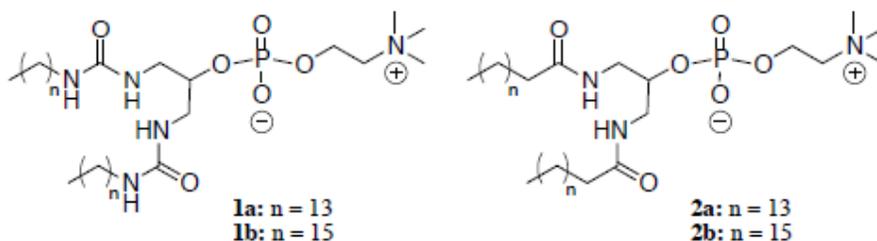
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Synthesis and characterization of artificial phospholipids

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Organic chemistry is an attractive tool to study the properties of phospholipid vesicles: by changing the key parts of phospholipid molecules a deeper understanding of the balance of physical forces at play can be gained. This is important for the optimization of the release properties of mechanosensitive liposomes (1).



Here, a new urea-type phospholipid **1** will be introduced. The synthesis as well as the monolayer and bilayer biophysical characterization of the bis-urea phospholipids **1a** and **1b** (2) will be compared to natural lipids as well as to the artificial 1,3-diamido phospholipids **2a** and **2b** (3).

- (1) M. N. Holme, I.A. Fedotenko, D. Abegg *et al.*, *Nat Nanotechnol* **2012**, 7, 531.
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Cononsolvency of PNIPAM at the transition between solvation mechanisms

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Poly-N-isopropyl acrylamide (PNIPAM) is a thermo-responsive polymer, which exhibits the rather rare phenomenon of cononsolvency (1). An example of this cononsolvency phenomenon is the behaviour of PNIPAM in water / methanol mixtures. At a fixed temperature of $T = 20^\circ\text{C}$ PNIPAM is perfectly soluble in both pure water and pure methanol, but it is insoluble in certain mixtures of the two solvents, as shown in Fig.1a. Directly correlating with the reentrant transition of soluble-to-insoluble-to-soluble, the PNIPAM dimensions change as a function of solvent composition, describing a reentrant coil-to-globule-to-coil transition (2), as schematically shown in Fig.1b.

We show that such phenomena can be understood as the result of a transition between solvation mechanisms. In water-rich environments, the solvation of PNIPAM is primarily determined by the enthalpic gain of water, solvating the polymer via hydrophobic hydration.

In alcohol-rich environments it is instead the gain in the mixing-entropy that determines solubility. Cononsolvency is observed in the transitional range between these two

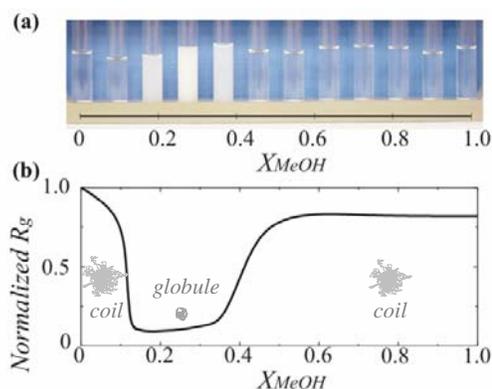


Figure 1: (a) Phase behaviour of PNIPAM in water/methanol mixtures as a function of the methanol molar fraction X_{MeOH} at a fixed temperature $T=20^\circ\text{C}$. (b) Schematic of the dependence of the radius of gyration R_g on methanol content obtained at a fixed temperature $T=20^\circ\text{C}$ (drawn from ref. (2)).

solvation mechanisms, where neither the gain in solvent enthalpy nor the gain in solution entropy is prevailing.

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(2) G.Zhang and C.Wu, **2001**. The water/methanol complexation induced reentrant coil-to-globule-to-coil transition of individual homopolymer chains in extremely dilute solution. *J.Am.Chem.Soc.* 123: 1376-1380.