Swiss Soft Days

9th Edition

Nestlé Research Center, Lausanne

Monday, October 29th 2012

Program

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Abstracts

Swiss Soft Days IX

29. October 2012, 10:00 to 17:30

Nestlé Research Center, Lausanne

10:00 – 10:20	Registration and coffee	
10:20 – 10:30	*Burbidge/Limbach (Nestlé)*	Welcome
Session I – Encapsulation		
10:30 – 11:10	*Philipp Erni (Firmenich)*	Soft Matter in Industry: Design and Characterization of Delivery Systems
11:10 – 11:30	*Philipp Chen (ETH Zürich)*	Design, Production and Tuning of Microcapsules Using Microfluidics
Session II – Complex fluids and glasses		
11:30 – 11:50	*Stefan Wolf (U. Bern)*	Deformation of Erythrocytes in Two-Dimensional Microchannels
11:50 – 12:10	*Majid Mosayebi (ETH Zürich)*	Reconciling Liquid-and Solid-like Aspects of the Glass Transition
12:10 – 13:15	Poster Session I	
13:15 – 14:10	Lunch	
Session III – Interfaces		
14:10 – 14:30	*Davide Calzolari (U. Fribourg)*	Nanoparticles at the Water-Oil Interface: X-Ray Determination of the Contact Angle
14:30 – 14:50	*Christof Aegerter (U. Zürich)*	Transition in the coarsening dynamics of three dimensional foams of different liquid fraction
14:50 – 15:10	*Marco Ramaioli (Nestlé)*	Powder wicking and its relevance for the dissolution of a food powder
15:10 – 15:30	*Patrick Rühs (ETH Zürich)*	Interfacial rheology of biofilms
15:30 – 16:20	Coffee and Poster Session II	
Session IV – Protein interactions		
16:20 – 16:40	*Tristan Bereau (U. Basel)*	Scoring multipole electrostatics in atomistic protein-ligand binding simulations
16:40 – 17:00	*Corinne Verbert-Nardin (U. Geneva)*	Anti-amyloidogenic effect of short single stranded nucleotide sequences
17:00 – 17:20	*Enrico Spiga EPF (Lausanne)*	Development of a coarse-grained force field for numerical simulations of proteins
17:20 – 17:30	*Burbidge/Limbach (Nestlé)*	Closing remarks
18:30 ...	Gathering at *Brasserie du Chateau*	

Soft Matter in Industry: Design and Characterization of Delivery Systems

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In this contribution we discuss examples of soft matter research relevant to industry, focusing on problems relevant to delivery systems for volatiles, nutritional ingredients, or pharmaceuticals.

Many flavor and fragrance compounds are hydrophobic liquids. Oil-in-water emulsions are essential components of delivery systems for those molecules, either as intermediate materials in encapsulation processes, or as final products, for example in beverage emulsions. Drop and particle sizes in flavor and fragrance emulsions span the full range of length scales of interest in various areas of soft matter research: from nanometers in microemulsions up to hundreds of micrometers in core/shell capsules. Moreover, oils in emulsions relevant for foods, consumer products or pharmaceutical applications are typically mixtures of compounds with a wide range of hydrophobicities and partition coefficients. Consequently, they tend to be compositionally unstable and undergo ripening due to inter-droplet gradients in the chemical potential. Liquid interfaces in volatile emulsions are therefore typically stabilized with amphiphilic polyampholytes. In many cases, those are biopolymers, including proteins, polysaccharides, and hybrids thereof.

Here, we discuss (i) the competition between spreading/coating and rheology for core/shell capsules made by phase separation, assessing the competition between interface physics and bulk hydrodynamics; (ii) the roles of bulk mass transfer and interfacial rheology in oil-in-water emulsions undergoing mass transfer; and (iii) the mechanics of core/shell capsules. We outline the consequences for the design of delivery systems for volatiles, nutritional ingredients or pharmaceuticals.

REFERENCES:

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Design, Production and Tuning of Microcapsules Using Microfluidics

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INTRODUCTION: Filled microcapsules are attractive delivery systems for applications in medicine, cosmetics, food and self-healing materials [1]. In our work, we produce microcapsules from double emulsion templates formed in microfluidic devices, which leads to a high degree of control over their size, composition and properties.

MICROFLUIDICS: In the microfluidic process, double emulsions are formed by dripping an aqueous liquid into an immiscible oil phase, which is in turn engulfed by another aqueous phase, thus forming water-in-oil-in-water emulsions [2]. By using acrylate monomers and a photoinitiator as the oil phase, we can consolidate it into a solid shell with UV irradiation.

This enables easy tuning of the microcapsules through the fluid flow rates, the device geometry and other variables, which in turn makes these systems more challenging to predict. To investigate these dependencies, we start from theoretical predictions for the size of double emulsions and present quantitative design maps that correlate parameters such as fluid flow rates and device geometry with the size and shell thickness of monodisperse polymer-based capsules produced in microcapillary devices [3].

CAPSULES: We produce highly monodisperse microcapsules with outer diameters of 70–250 µm and shell thicknesses of 5–50 µm (see Fig. 1).

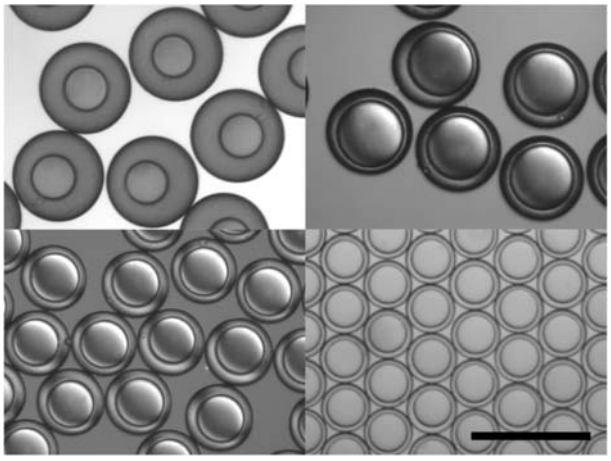

Fig. 1: Different capsules made in microfluidic devices. The scale bar represents 250 µm and applies to all pictures. [3]

Using polymers with selected glass transition temperatures as the shell material, we show through single capsule compression testing that hollow capsules can be prepared with tunable mechanical properties ranging from elastomeric to brittle. Weibull statistical analysis is performed on brittle capsules to evaluate the variability of the microfluidic route and assist the design of capsules in applications involving mechanically triggered release.

We also show that the permeability of the capsules can be tailored through the choice of polymer and addition of cross-linkers or plasticizers.

Finally, we can manipulate the microstructure of the capsule shell by using silica nanoparticles with different surface treatments in the middle phase of the double emulsion templates. This can range from homogeneous composite shells to layered structures, where the particles occupy only the outer and inner surfaces of the shell, allowing for subsequent surface modification of the entire capsule.

CONCLUSIONS: The microfluidic approach enables the production of monodisperse capsules with specific size, shell thickness, mechanics, permeability and also microstructure. With the quantitative and qualitative relations investigated in this work, we expect to expand the range of microcapsules that can be produced using this technique for a variety of existing and emerging applications.

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Deformation of Erythrocytes in Two-Dimensional Microchannels

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ARTORG Center, University of Bern, Bern, Switzerland.

INTRODUCTION: The perfusion in muscle tissue is more than one order of magnitude smaller compared to the perfusion rate in the kidney. This is caused by smaller capillary diameters in muscle tissue. As erythrocytes pass through capillaries and slits of similar diameters to that of their own equilibrium shape, they undergo huge deformations. These deformations have been studied in-vivo[1] and in-vitro[2]. Not only pathologies such as sickle cell anemia, but also red blood cell (RBC) aging, are connect to a decreased deformability of the red blood cells. We studied these deformations in an asymmetric microchannel and bifurcating channel where the fluid-cell interactions caused an asymmetry at the bifurcation's entrance. Our question is, what cytoplasm flow can be seen during asymmetric deformations in a microchannel.

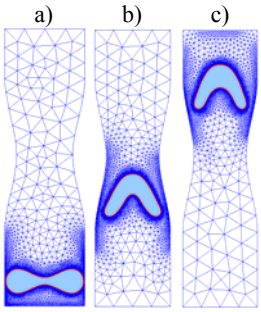

Fig. 1: Deformation of red blood cells passing a narrowing section in a two-dimensional micro-channel. From the biconcave equilibrium shape the erythrocyte deforms into a parachute shape. The geometry is remeshed, when the smallest element quality, that is ratio of the side length compared to an equilateral element, drops below 0.5.

METHODS: We used the finite element method and coupled the cell membrane with the cytoplasm and the surrounding fluid to simulate the geometries, see Fig 2. Both fluids viscosities were assumed to be Newtonian. The large deformations were handled using a moving mesh and mesh quality based remeshing, see Fig 1.

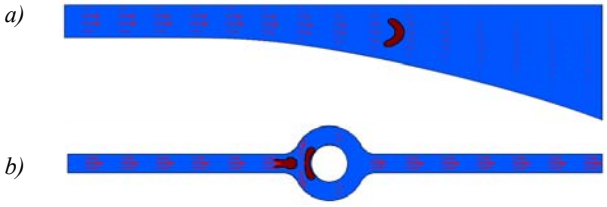

Fig. 2: Deformed red blood cells in microchannels of 100µm functional length. The asymmetric flow either is induced by the channel shape, a) or, by a flow-instability caused by the interaction of two erythrocytes in a symmetric bifurcating channel as in b).

The membrane is considered to be a homogenous material of 10nm thickness with isotropic linear shear elastic moduli 6.3 µN/m. We assumed the outer fluid to be similar to blood plasma, the density was 1.025kg/m^3 and viscosity was 1.2mPa s. The values for the cytoplasm were density 1120kg/m^2 and viscosity 1.6mPa s.

RESULTS: In all two cases we applied an entrance pressure of 10Pa and an exit pressure of 0Pa. The first channel design, the opening channel, deflects the cell, see Fig 2a. The cell almost stays in the center of the flow, and deforms similar to the symmetric parachute. Due to the asymmetry of the opening, the slow inner flow is asymmetric, see Fig 3a. Finally, in the symmetric bifurcating channel the cells maintains a symmetric shape, and the first cell is draped at the bifurcation, see Fig 2b. When the second cell enters that then constricted section, the flow becomes unstable and asymmetric. This asymmetry then frees the draped first cell and an asymmetric inner flow can be observed, see Fig 3b.

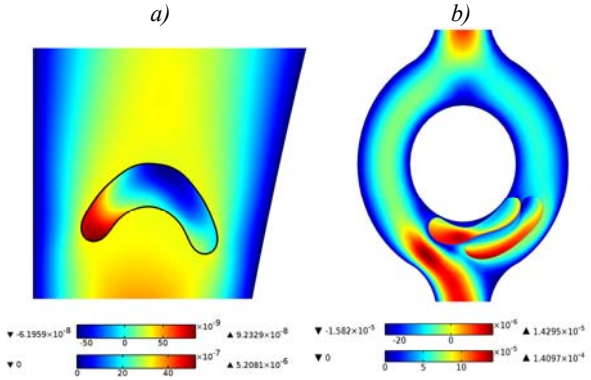

Fig. 3: Asymmetric flow patterns in the RBC's cytoplasm and in the outer fluid, using Newtonian behavior for the cytoplasm. In all cases the initial shape and flow were symmetric. The cytoplasm velocity, in m/s, is given by the upper scale in and the surrounding fluid's velocity, in m/s, is given by the lower scale.

DISCUSSION & CONCLUSIONS: We studied the inner flow of red blood cells in asymmetric flows assuming Newtonian fluids and a viscosity difference between the inner and outer fluid. Considering a non-linear viscosity for the cytoplasm and slightly smaller cell, as it is observed in aged red blood cells, will change the cells deformation deflection and may serve for size sorting of RBC.

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RECONCILING LIQUID- AND SOLID-LIKE ASPECTS OF THE GLASS TRANSITION

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INTRODUCTION: Whether the glass transition can be understood on the basis of a purely dynamical crossover without any thermodynamic signature or whether it requires a thermodynamic or structural origin, represents a central question in the field of glass-forming liquids. Recently we showed [1,2] that deformation of inherent structures -that are local minima of the underlying potential energy landscape- could be a powerful tool for detecting structural changes and the onset of cooperativity in supercooled liquids. In this computational study we will investigate the correlations between the non-affine displacements of inherent structures and the dynamical heterogeneities.

METHODS: We use small static deformations to perturb inherent structures and to extract non-affine displacements by comparing them before and after deformation [2]. We characterize the dynamical heterogeneities of the initial configurations by calculating the local Debye-Waller factor. Local Debye-Waller factor of each particle is the iso-configurational average of the variance of its position during a fixed time interval corresponding to the short time, β-relaxation regime. Finally, for different inherent structures, we also perform normal mode analysis by diagonalizing the Hessian matrix.

RESULTS: Our results suggest that in supercooled liquids there are significant spatial correlations among the non-affine displacements, the local Debye-Waller factors and the spatial organization of quasi-localized soft normal modes [3] (see e.g. Fig. 1). These correlations decrease by increasing the temperature or deformation magnitude. Normal mode analysis of our configurations also reveal that while the Debye-Waller factor is better predicted by the mode map when a larger number of soft modes are included, non-affine displacements are very much correlated to the mode map when only a few lowest-frequency soft modes are considered.

DISCUSSION & CONCLUSIONS: We showed that particles dominating dynamical heterogeneities are those responsible for substantial non-affine displacements. These particles are mostly participating to quasi-localized soft normal modes. Furthermore, we could clarify that among soft normal modes, those of intermediate frequencies tend to dominate dynamical heterogeneities, whereas the few lowest modes, that also control the mechanical stability of amorphous solids [4], determine the largest non-affine displacements. The correlations between dynamical heterogeneities and non-affine displacements arise from the strong similarities in the spatial distributions of soft modes of nearby inherent structures, accessible via small amplitude deformations. By increasing the deformation amplitude beyond a threshold, the two soft mode distributions become very different and therefore such correlations decrease significantly.

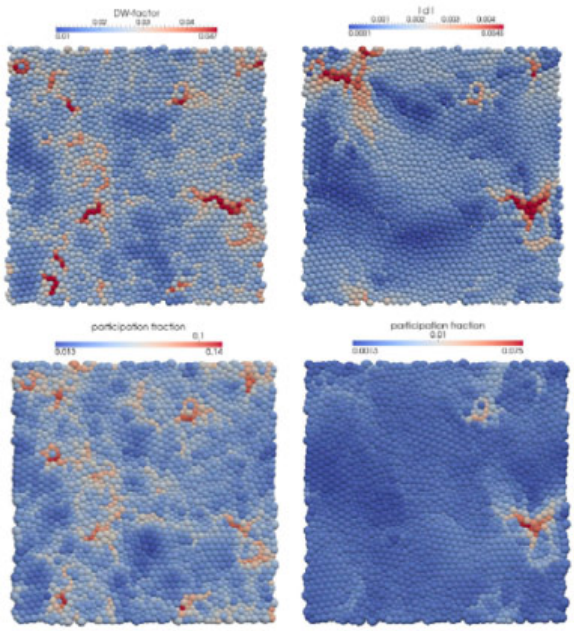

Fig. 1: (top) Maps of local DW factor (left) and magnitude of non-affine displacements for small deformation (right) plotted for the same initial configuration. (bottom) Maps of participation fraction of particles to quasi-localized soft modes when the first 60 modes (left) and 7 modes (right) are included.

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Nanoparticles at the Water-Oil Interface: X-Ray Determination of the Contact Angle

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INTRODUCTION: Self-assembly of nano-particles (NPs) at liquid-liquid interfaces is of fundamental scientific interest[1,2] and great technological impact.[3,4] It is, therefore, intensely studied both theoretically[5] and experimentally.[6] Accurate measurements of the NP's contact angle Θ (Figure 1(a)) and binding energy Δ*E* are very challenging, particularly for NPs residing at deeply buried interfaces between immiscible liquids. We report x-ray based Θ measurements and classical ΔE calculations for silica nanoparticles (NPs) adsorbed at a flat interface between hexane and aqueous solutions of cetyltrimethylammonium bromide (CTAB) surfactant.

METHODS: The NP film interfacial structure is determined with Ångström resolution by high-energy (70 keV) x-ray reflectivity (XRR) for two CTAB concentrations, Φ_c, well below and near the critical micelle concentration, Φ_{cmc}.
For the analysis of the experimental XRR profiles we have developed a physically motivated model in which the fitting parameters are directly related to the main structural properties of the interface. From the fitted average NP water immersion h_{av} the contact angle is readily calculated as $\Theta=\arccos(-1+ h_{av}/r_{av})$, where r_{av} is the average NP radius obtained by SAXS. The binding energy is obtained via the classical formula $\Delta E=\pi\gamma(h_{av})^2$, where γ is the equilibrium tension of the NP-loaded water-oil interface.

RESULTS: At low Φ_c (0.05 mM) we find a dense monolayer (ML) of close-packed NPs with $\Theta = (146\pm4)^\circ$, while higher Φ_c (0.75 mM) yields a less dense ML with lower $\Theta = (128\pm6)^\circ$. The NP close-packing scenario suggests a solid-like character for the low-Φ_c ML, which is likely stabilized by strong inter-NP interactions that are neglected in the standard Δ*E* calculation. The latter yields (24±10)kT and (5±2)kT for the high and low Φ_c systems, respectively[7].

DISCUSSION & CONCLUSIONS: The low ΔE obtained at low Φ_c contrasts starkly with the highly stable, close-packed XRR-determined monolayer advanced interfacial binding theories, particularly

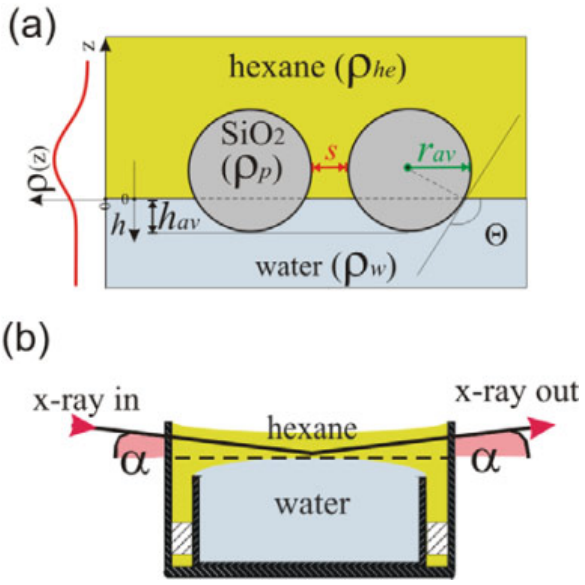

Fig. 1: Schematic representation of two spherical particles at the water-oil interface with main physical model parameters. (b) Sketch of double beaker sample environment for hard X-ray reflectivity experiments.

in the case of dense MLs of interacting nano-sized particles. We hope that this experimental study will motivate novel theoretical and simulation work leading to a deeper understanding of the energetics, formation, and hydrophobicity-related properties of these technologically important nano-scale multi-component interfaces.

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Transition in the coarsening dynamics of three dimensional foams of different liquid fraction

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INTRODUCTION: We study diamagnetically levitated foams with different liquid fraction. Due to the levitation, drainage is effectively suppressed and the dynamics is driven by the coarsening of the foam bubbles. For dry foams, the bubble size increases as the square root of foam age, as is expected from a generalized von Neumann law. At higher liquid content, the behavior changes to that of Ostwald ripening where the bubbles grow with the 1/3 power of the age. Using diffusing wave spectroscopy we then study the local dynamics in the different regimes and find diffusive behavior for dry foams and kinetic behavior for wet foams.

METHODS: In order to assess the growth of the foam bubbles with age inside the three dimensional foam, we use multiply scattered light transmitted through the foam. In addition, the diffuse light can be used to obtain information on the averaged local dynamics of the foam.

The foams used in the experiments consist of water, sodium dodecyl sulfate (SDS) as a surfactant and N_2 gas. The liquid content in the foam is determined by the volume-ratio of water-SDS mixture and gas in the initial state within the two syringes. The foam thus created is then transferred to a sample-cell, which is placed inside the room temperature bore of a superconducting magnet capable of applying a field of 18 T. The magnet is a solenoid at the end of which, the field shows a substantial gradient. Due to the field distribution, this will lead to a stable levitation at this point [1], where the levitation will be homogeneous to one part in a thousand within a volume of 1 cm^3, thus for almost the whole foam sample. This levitation force exactly compensates gravity, which would lead to drainage of the foam, thus opening up the possibility of directly studying coarsening in a three dimensional foam over long times and at different liquid fractions.

RESULTS: We have shown the existence of a transition in bulk coarsening dynamics in three dimensional foams at a liquid fraction of 30 %. At lower liquid fraction, the coarsening dynamics is governed by a von Neumann law [2], which corresponds to a growth of the average bubble size with the square root of time. At higher liquid content, the bubbles grow via Ostwald ripening [3], i.e. the average bubble size growth with time to the power of 1/3. The difference in coarsening dynamics is driven by the fact that at low liquid content the bubbles are in close contact thus changing the nature of gas transport between bubbles.

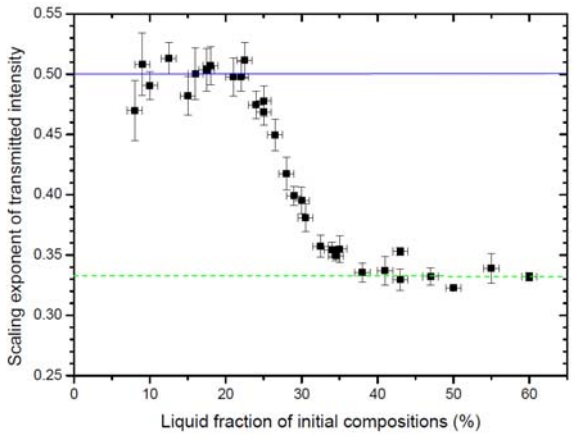

Fig. 1: Power of the coarsening dynamics as a function of foam liquid fraction.

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Powder wicking and its relevance for the dissolution of a food powder

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Upon pouring a soluble powder onto the surface of water, to reconstitute a beverage, several phenomena condition the quality of the beverage obtained.
We present a model impregnation problem, which is relevant to shed more light on some aspects of this complex process.
Spontaneous impregnation of non-soluble powder layers at the surface of a liquid is studied [1], showing the existence of a critical contact angle below which impregnation occurs. The dependence of the impregnation condition on grain polydispersity and applied pressure is also discussed.
Finally, these observations are linked to the wetting of soluble powders [2], deriving upper bounds for their wicking velocity.

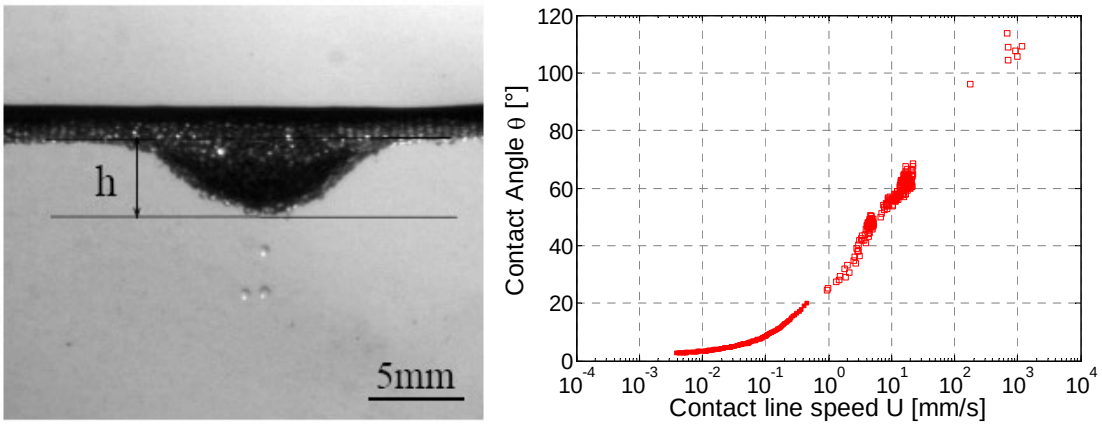

Fig 1 Left: Effect of the hydrostatic pressure on the impregnation condition of non-soluble grains.
Right: Dynamic wetting angle on a maltodextrin thin layer.

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Interfacial rheology of biofilms

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The transient build-up of air-water bacterial biofilms is measured by interfacial rheology. Biofilms are highly complex structures composed of bacterial cells embedded in an extracellular polymeric matrix. Biofilm formation in food industry is especially critical as these can lead to food poisoning and outbreaks caused by pathogens such as *Escherichia coli* and *Listeria monocytogenes* [1-3]. Interfacial rheology on biofilms is proposed to study the influencing environmental factors such as pH, temperature, and presences of surfactants that influence the formation and the destruction of biofilms.

Biofilm forming bacteria such as *Bacillus subtilis, Escherichia coli,* and *Pseudomonas fluorescens* were chosen as model bacteria. To measure the interfacial rheology of water-air biofilms, we use the subphase interfacial rheological setup, which is able to measure the effects of external triggers on the biofilm without destroying the interface [4]. With this method the influence of e.g. solvents or pH changes on the biofilm formation and development can be observed through the interfacial elastic and viscous moduli. To support the observed structural changes, dilatational rheology was performed with a pendant drop tensiometer.

The biofilm growth for *B. subtilis*, *P. fluorescens* and *E.coli* is depicted in Figure 1. Complex biofilm growth behaviour was observed through increasing and decreasing interfacial moduli over time.

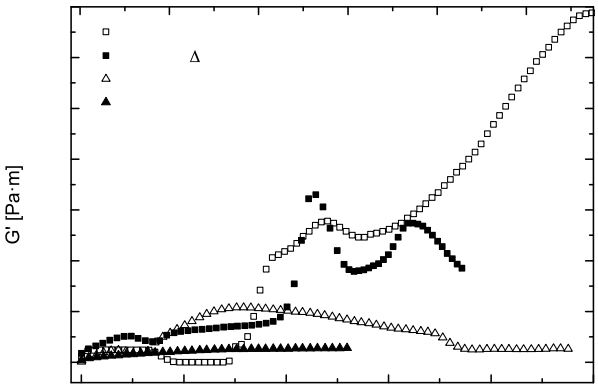

Figure 1: The transient development of the elastic interfacial modulus G' of B. subtilis, E. coli P. fluorescens, and LB media, at 25°C.

In Figure 2 the influence of pH on the interfacial network strength was measured. The network, consisting of proteins, was especially sensitive to pH changes as observed in the elastic modulus G'.

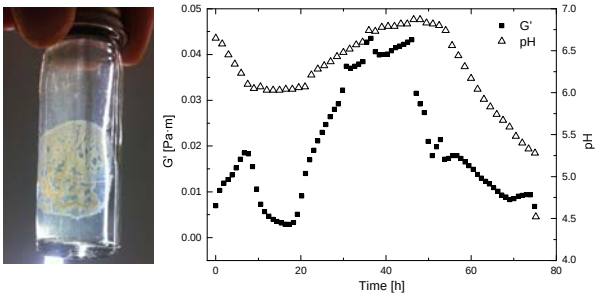

Figure 2: Biofilms formed by bacillus subtilis (left) at 25°C in LB broth were tested on their pH influence through subphase controlled interfacial rheology.

Interfacial rheology proved to be a valuable tool for studying biofilms as the influence of temperature, media type, bacterial strain, pH and surfactant concentration could be observed successfully during biofilm formation.

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Scoring multipole electrostatics in atomistic protein-ligand binding simulations

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The incorporation of fluorine in pharmaceutical products has enjoyed growing interests due to its ability to improve protein-ligand binding, metabolic stability, and modulate physicochemical properties, e.g., lipophilicity, basicity. While the effects of fluorine are relatively well understood [1], an accurate determination of the energetics of specific protein-ligand interactions still call for quantitative studies. In this regard, a computational approach provides both atomistic resolution and a decomposition of the interactions at hand.

In this work, we study the effects of degrees and patterns of fluorination on the binding affinity of various inhibitors with carbonic anhydrase II. The method is validated by comparing free-energy calculations with experimentally determined binding affinities—similar to a previous study of non-fluorinated ligands [2].

While the computational power at hand limits these simulations to a point-charge (PC) representation of the electrostatics, we evaluate the effects of multipole (MTP) interactions on the ligand by scoring PC-sampled conformations with a MTP energy function. The protein-ligand free energies are re-evaluated with the more detailed force field to assess the increased accuracy with respect to the experimental values. A careful and consistent parametrization of the two force fields yields encouraging results. Gaining insight from a MTP representation holds many promises to provide a detailed decomposition of the multipolar interactions that drive protein-ligand binding.

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Anti-amyloidogenic effect of short single stranded nucleotide sequences

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INTRODUCTION: To induce the self-assembly of nanostructures that are potentially biologically active, we have undertaken investigations of the structure formation and modes of interactions of macromolecules resulting from the coupling between a short, nucleotide long sequence and a hydrophobic block[1,2]. Interestingly covalent coupling of the diphenylalanine (FF) dipeptide with a twelve nucleotide long sequence induces a morphological transition from the pristine FF tubular structures to hollow spheres[1]. Although FF is a common peptide motif of the amyloid peptide sequences identified in diseases such as Parkinson's, Alzheimer's and some types of diabetes, we observed that unlike with FF, co-incubation of the amyloidogenic peptide with nucleotide sequences induces the formation of homogeneous micrometer size soft spherical structures (Figure 1).

METHODS: Conventional characterization techniques have been used to characterize the morphology of the structures resulting from the incubation of amyloidogenic peptide and nucleotide sequences. Optical (see Figure 1 for a typical example) and atomic force microscopy have been combined to electron microscopy to assess the morphology of the resulting structures. The classical tinctorial properties of amyloid deposits, including the birefringent red-green staining achieved with Congo Red and the fluorescent dye shifts observed with thioflavins have been used to assess the kinetics of fibrils formation by spectroscopy.

RESULTS: Nucleotide sequences might interact with amyloidogenic peptides through several binding modes such as electrostatic interaction or intercalation. However, incubation of the amyloid fibers in an electrolyte solution (sodium chloride) does not affect the formation of the fibrils. Similarly, incubation with single nucleotides is not sufficient to induce the disruption of the amyloid fibrils.

Being a nucleotide sequence composed of the bases linked by sugar and phosphate backbones connected through ester bonds, this latter observation evidences that a fine cooperative balance between electrostatic and hydrophobic interaction that depends on the composition and length of the nucleotide sequence induces the amyloid fibrils disruption upon incubation with nucleotide sequences.

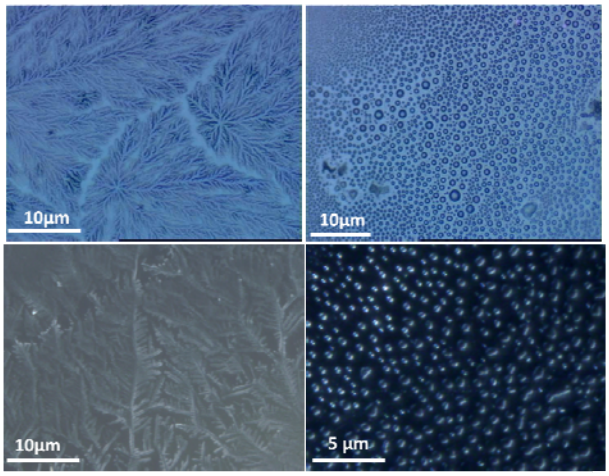

Fig. 1: Bright field (and corresponding dark field) optical microscopy (50X magnification): (a, c) 3 days aged amyloid fibres (0.01 mgmL-1) in 5mM PBS at PH 7.5; (b, d) Fibres were incubated with 0.1 mg 12-mer nucleotide long sequences for 1 h at 37 °C, amyloidogenic peptide to nucleotide sequence ratio 1:8.

DISCUSSION & CONCLUSIONS: As a result from these preliminary observations we came to the hypothesis that incubation of the amyloidogenic proteins with the nucleotide sequences leads to an interpolyelectrolyte complex (IPEC) of the misfolded intermediate form of the amyloidogenic peptide upon electrostatic and hydrophobic interaction with the nucleotide sequences. This hypothesis is further supported by atomic force microscopy, which demonstrates that the resulting structure that is formed by co-incubation of nucleotide sequences and amyloidogenic peptides is a soft material, which is currently under investigation.

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ACKNOWLEDGEMENTS: K. Adea and Dr. Bauer are gratefully acknowledged for their technical and scientific support.

Development of a coarse-grained force field for numerical simulations of proteins

Coarse-grained (CG) molecular simulations have been extensively used in the last decade to investigate the structure and dynamics of biomolecules. The softer nature of the potential terms allows to sample size and time scales which are significant larger than those accessible by atomistic models. We present here the ongoing development of a non-radial CG model for molecular dynamics simulation of proteins, which, differently to current CG approaches, accounts for the dipolar electrostatic contribution of the backbone and side-chains. CG models holding such simplified description of the electrostatics are able to accurately describe the atomistic electrostatics field and naturally stabilizes secondary structure motifs. Our model maps roughly four heavy atoms to one CG bead, and the adopted parametrization strategy is based on a Boltzmann inversion of selected degrees of freedom extracted from all-atom simulations, and a final all-atom MD-based force-matching procedure using a global optimization algorithm. The first generation of this CG force field has been used to test the dynamic determinants of a set of proteins with α-, β-fold and for small protein-protein complexes, showing promising results for the study of molecular recognition in large protein-protein assemblies.

High-sensitivity diagnosis of malaria via magnetically induced linear dichroism

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INTRODUCTION: Although malaria infection is a global health issue, a cost-effective, yet highly sensitive diagnostic method has not been developed. We aim to design a compact and inexpensive clinical diagnostic device that could be operated without any expertise in the field of medicine or engineering. The principle of the detection – first suggested by Newmann and coworkers [1] – is the measurement of magnetically induced linear dichroism exhibited by malaria pigment (also known as hemozoin crystals), which is present in human blood only if infected by malaria parasites.

These micrometer-size crystals are an appropriate target of diagnosis owing to their unique properties. As a consequence of their low-symmetry crystal structure and elongated shape, they exhibit large linear dichroism and magnetic anisotropy [2]. When suspended in blood, the magnetic anisotropy enables the single crystals to be orientated along their easy axes by an external magnetic field. This co-aligned ensemble of the dichroic crystals shows macroscopic linear dichroism for polarization along and perpendicular to the direction of the magnetic field. We studied this effect over the near infrared- ultraviolet region using a polarization modulation technique along with magnetization measurements via SQUID.

METHODS: The spectrometer capable of the measurement of MLD over the wavelength range of λ=180-1300nm was assembled using a triple grating monochromator, broad-band light sources (Xearc and tungsten lamps) together with a photomultiplier and an InGaAs photodiode as detectors. The experiment was set up in Voigt configuration, that is the magnetic field was applied perpendicularly to the direction of the light propagation. The fast switching between the light polarizations parallel and perpendicular to the magnetic field was carried out with a fused silica photoelastic modulator operating at a frequency of 50 kHz.

As a more suitable alternative for diagnostics, we replaced the polarization modulation with a rotating magnetic field that forces hemozoin crystals to act like spinning polarizers. This concept - realized by a cheap laser diode, a Halbach array magnet, a Rochon prism and a balanced photodiode bridge – provides an unprecendented sensitivity in the detection of malaria pigment corresponding to the minimal concentration of 0.5 ng/ml in blood plasma.

RESULTS: Using the polarization-modulation spectrometer we revealed fundamental information on hemozoin crystals including their broad-range (UV-NIR) spectrum of magnetically induced linear dichroism (see Figure) – which may serve as a unique fingerprint of the crystals – and the value of the magnetic anisotropy at room temperature, which allows them to be oriented in a liquid thus providing a sensitive way of diagnosing malaria.

We assembled a prototype of the diagnostic tool capable of detecting ultra-low concentration of hemozoin crystals suspended in blood plasma (0.5ng/ml).

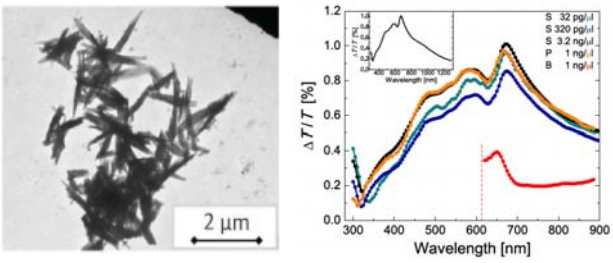

Figure: (left): Transmission electron micrograph of hemozoin crystals.
(right) : Magnetically induced linear dichroism spectrum of hemozoin crystals suspended in normal saline (S), blood plasma (P) and blood (B) over the NIR-UV wavelength domain.

DISCUSSION & CONCLUSIONS: Though experiments on malaria-infected blood samples and field tests have not been performed so far, the high sensitivity of our device confirms the possible feasibility of diagnosis based on this cost-effective methodology.

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An Electrical Method To Quantify Nanoparticle Interaction With Lipid Bilayers

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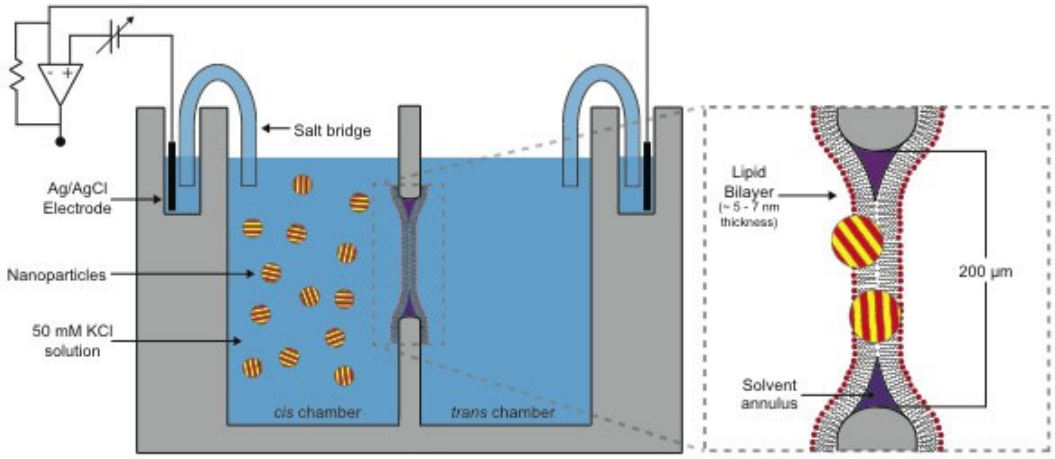
Abstract

Understanding as well as rapidly screening the interaction of nanoparticles with cell membranes is of central importance for biological applications such as drug and gene delivery. Recently, we have shown that 'striped' mixed-monolayer coated gold nanoparticles spontaneously penetrate a variety of cell membranes through a passive pathway. Here, we report an electrical approach to screen and readily quantify the interaction between nanoparticles and bilayer lipid membranes. Membrane adsorption is monitored through the capacitive increase of suspended planar lipid membranes upon fusion with nanoparticles. We adopt a Langmuir isotherm model to characterize the adsorption of nanoparticles by bilayer lipid membranes and extract the partition coefficient, K, and the standard free energy gain by this spontaneous process, for a variety of sizes of cell-membrane penetrating nanoparticles. We believe that the method presented here will be a useful qualitative and quantitative tool to determine nanoparticle interaction with lipid bilayers and consequently with cell membranes.



BLM electrophysiology. Two compartments (*cis* and *trans*) are separated by a small aperture that is 200 µm in diameter, onto which the bilayer lipid membrane is formed. The compartments are each filled with an electrolytic solution and connected to electrodes via salt bridges. A membrane potential is applied and the current is amplified using a voltage-clamp amplifier. Increasing concentrations of nanoparticles are then added to the *cis* compartment and the current/capacitance is monitored by stepped magnitude increases of the square wave due to the insertion of individual NPs into the membrane.

Self-Shaping Composites with Programmable Bioinspired Microstructures

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INTRODUCTION: Shape change is a prevalent function apparent in a diverse set of natural structures including seed dispersal units, climbing plants, and Venus flytraps. Many of these natural materials change shape by using cellulose microfibrils at specific orientations to anisotropically restrict the swelling/shrinkage of their organic matrices upon external stimuli. This is in contrast to the material-specific mechanisms found in synthetic shape-memory systems. Here, we propose a facile, robust and universal method to replicate this unusual shape-changing mechanism of natural systems in artificial bioinspired composites. The technique is based upon the remote control of the orientation of reinforcing inorganic particles within the composite using a weak external magnetic field. Combining this reinforcement orientational control with swellable/shrinkable polymer matrices enables the creation of composites whose shape change can be programmed into the material's microstructure rather than externally imposed. Such bioinspired approach can generate composites with unusual reversibility, twisting effects and site-specific programmable shape changes.

METHODS: We present a synthetic framework for building autonomous self-shaping composites in which the shape change is programmed within the microstructure of 3D macroscopic objects by controlling the local orientation of stiff reinforcing elements in a swellable/shrinkable surrounding matrix. To gain control over reinforcement architectures, we exploit the Ultra-High Magnetic Response (UHMR) exhibited by discontinuous, anisotropic reinforcement microparticles coated with superparamagnetic iron oxide nanoparticles (SPIONs) [1]. By applying weak external magnetic fields, reinforcement particles can be oriented into architectures akin to these natural systems or into a wide range of completely unique and programmable shape-changing microstructures.

RESULTS: Using our technique, we gain the ability to position anisotropic reinforcement particles both orientationally and spatially in gelatin and PNIPAAM matrices [2]. These systems have structures and anisotropic swelling that mimic natural systems. These include the following: 1) in-plane reinforcement leading to swelling with high anisotropy (*plant stems*); 2) simple bilayer reinforcement leading to curled swelling (*pinecones*); 3) orientationally unique bilayers that swell into helical configurations (*orchid tree seed pods*). Further, we demonstrate that shape change can be reversibly instigated with various mechanisms from hydration to temperature. This work offers a way forward in recreating these defined reinforcement architectures within manufactured polymers.

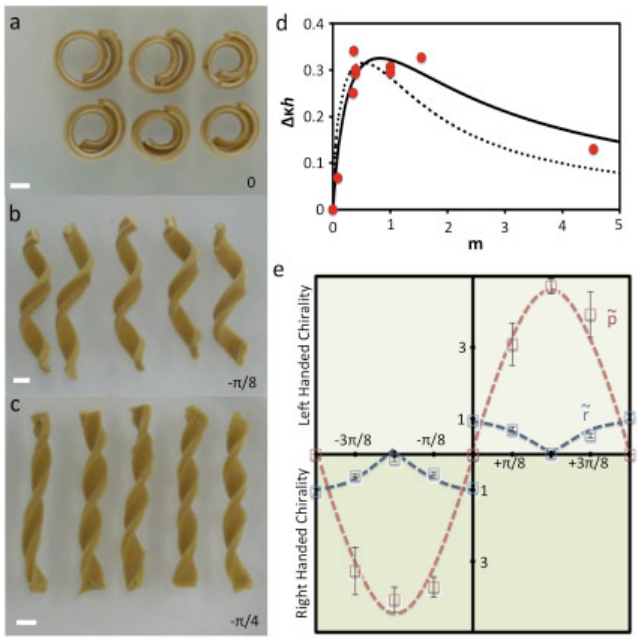

Fig. 1: (a-c) Shape change in synthetic monolithic materials that mimic reinforcement orientations of a chiral seedpod. (d,e) Experimental data are well described by theoretical predictions (lines).

DISCUSSION & CONCLUSIONS: Synthetic hydrogel composites can be made that self-shape into programmed configurations upon external stimuli using the bending and twisting mechanisms exhibited by pinecones, wheat awn structures, and orchid tree seedpods. Such bioinspired architectures can be recreated in synthetic systems by controlling the orientation of UHMR microplatelets using low magnetic fields. Focusing on microstructural design allows this technique to extend to any composite system comprising of anisotropic reinforcing elements surrounded by a matrix that undergoes significant dimensional changes upon a given external stimuli.

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Biopolymer-based core/shell capsules: colloidal interactions, interfacial physics and barrier properties

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Core/shell capsules with biopolymer walls are relevant in a many applications including flavors, perfumes, pharmaceuticals, or inks. Encapsulation systems that combine a 'label-friendly' wall chemistry and ease of applicability or low material and processing costs are particularly interesting. For flavor applications, the choice of wall materials is naturally restricted to edible ingredients in line with legislation constraints; self-assembled, biopolymer-based capsules with coacervate shells are among the most important delivery systems in this field.

Complex coacervation is a liquid/liquid phase separation occurring in colloidal systems, resulting in the formation of two liquid phases: a hydrocolloid-rich phase (coacervate phase) and a dilute continuous phase. The coacervate appears as amorphous liquid droplets exhibiting affinity for interfaces due to specific interfacial properties.

Whereas the phase separation aspect has been covered in much detail in the literature, less quantitative knowledge is available on the subsequent steps in microcapsule formation, including emulsification/dispersion of the active ingredient, deposition and coalescence of coacervate nodules onto the active/continuous phase interface, physical gelation and, optionally, covalent crosslinking of the wall.

Here, we investigate complex coacervation from the perspective of delivery systems, focusing on the intimate coupling of phenoma including colloidal interactions and phase diagrams, the hydrodynamics of core formation, and quantitative analysis of crosslinking in the wall material. Methods include microscopy, dynamic and static light scattering, rheology, and micro-DSC.

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CO_2 permeabilities of AQPs in artificial lipid and polymeric vesicles

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Whether certain AQPs serve as CO_2 channels, and thereby play a physiological role, remains controversial, because lipid membranes are naturally highly permeable to gases (1). Therefore, the use of artificial membranes that have low background permeabilities to CO_2 (P_{CO2}) make it possible to show that AQPs serve as CO_2 selective channels. Here, we use two artificial membrane systems, one based on the triblock copolymer polymethyloxazoline - polydimethylsiloxane (PMOXA-PDMS-PMOXA), and one based on lipid cholesterol mixtures, to measure the P_{CO2} by the ^{18}O technique (2) for two different AQPs, hAqp1 and bacterial AqpZ. We demonstrate that high concentrations of cholesterol (~50 mol-%) in lipid vesicles decreases the P_{CO2} of control vesicles drastically, making them well suited for measuring P_{CO2} through AQPs in order to compare them to biological membranes, e.g. red blood cells (3). We can also calculate single-channel permeabilities of AQPs by using the freeze fracture technique on AQP-containing lipid vesicles. In addition, reconstituting membrane proteins in artificial triblock copolymer vesicles (4, 5) – which have even greater chemical and mechanical stability and lower intrinsic CO_2 permeability than lipids – makes such artificial membranes an ideal system to study gas permeabilities for different kinds of membrane proteins.

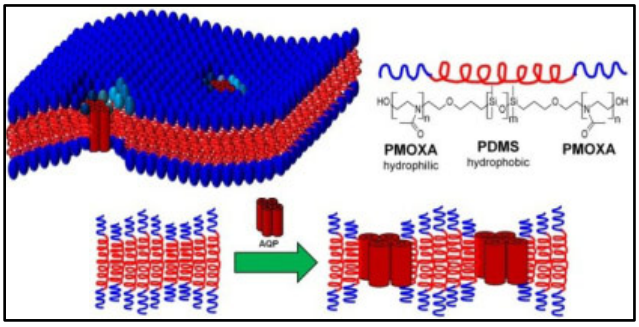

Figure 1: Illustration of our polymeric membrane with reconstituted membrane proteins, and the triblock copolymer chemical formula.

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Towards a constitutive model for the rheology of supercooled liquids

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The nonequilibrium dynamics of glassy systems pose several challenges due to their long relaxation times and the large time scale gap between micro- and macroscopic dynamics. Guided by general principles of nonequilibrium thermodynamics we develop a constitutive model which should enable us to describe the characteristic behavior of supercooled liquids on a macroscopic scale. We want to base our model on recent results obtained in our group by investigating the non-affine response of a liquid's inherent structure subject to external shear.

We analyzed the non-affine response employing image processing techniques, which revealed the presence of local correlations. As temperature is decreased, these correlations grow in size while their number is decreasing. Frequently, a disproportionally high change of local potential energy at their boundaries can be observed. These preliminary results indicate their importance for a description of the system's macroscopic, rheological state.

Gene Expression in Synthetic Micro- and Macro-Tissues

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INTRODUCTION: Tissue-engineering utilizes living cells seeded into artificial structures [1, 2]. Assemblies of artificial vesicles may provide a promising new building material for tissue-engineering, where encapsulated and spatially organized active substances and genetic programs nourish the growth, control the proliferation, and/or induce the differentiation of seeded cells in a smart and time-dependent way.

Here, we demonstrate the bottom-up synthesis of biomimetic two-dimensional artificial micro- and macro-tissues composed of giant unilamellar vesicles (GUVs). The programmable adhesive properties of DNA oligonucleotides thereby defined the vesicles' connectivity and spatial arrangement. Additional cell- and tissue-like properties arose from the encapsulation of a complex biological machinery enabling in vitro gene expression.

METHODS: Three GUV populations were prepared using the water-in-oil emulsion transfer [3]. *Fig.1A* details the vesicle functionalization. The surface functionalization protocol is reported elsewhere [4].

RESULTS & DISCUSSION: *Fig.1B* shows representative examples of biomimetic two-dimensional artificial macro- and micro-tissues of defined connectivity and spatial arrangement. Assembled vesicles are clearly distinguishable by their deviation from the circular shape and the extensive contacts they form with adjacent vesicles functionalized with complementary DNA oligonucleotides. In *Fig.1C* only connected vesicles are shown. The mutual complementarity of the three GUV populations ensures an unlimited self-assembly process consequently resulting in two-dimensional macro-tissues. On the other hand, binary assemblies resulting from the exclusion of either GUV population 1 or 2 through a non-complementary ssDNA address not only show the specificity of the self-assembly process, i.e. the gene expressing vesicles of population 3 assembled exclusively with only one of the other two vesicle populations, but also show the self-assembly process to undergo self-termination consequently resulting in two-dimensional micro-tissues.

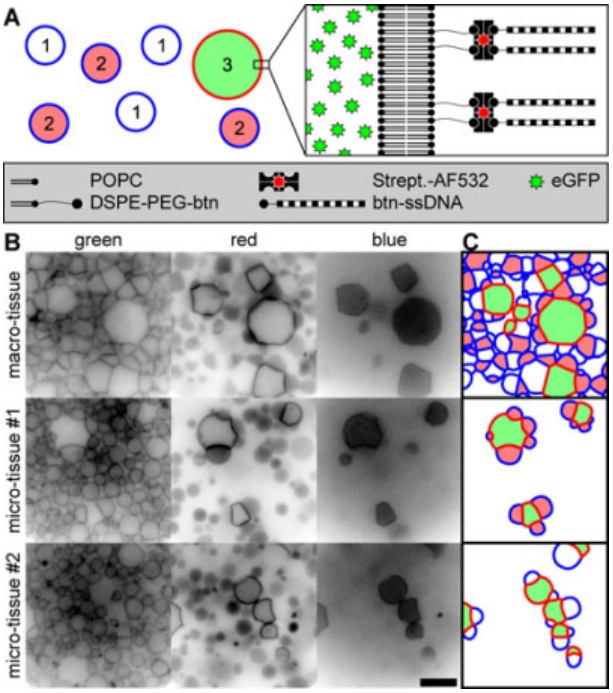

Fig. 1: ***A)*** *Scheme of the functionalization of the three vesicle populations (1, 2, 3). Fluorescent streptavidin Alexa Fluor conjugates were used to anchor biotinylated ssDNA oligonucleotides to biotinylated phospholipids (DSPE-PEG-btn) incorporated into a POPC-phospholipid bilayer. Encapsulation of an E.coli-based cell-free expression system allowed the synthesis of fluorescently active enhanced green fluorescent protein (eGFP).* ***B)*** *Fluorescence micrographs of ternary (macro-tissue) and binary (micro-tissues) assemblies of artificial giant unilamellar vesicles. Scale bar: 20 µm.* ***C)*** *Scheme of the connectivity of the assembled vesicles of panel B. Only assembled vesicles are shown. The self-assembly process of the micro-tissues was self-terminating resulting in binary assemblies of limited dimension.*

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Mapping thiolate monolayers on gold nanoparticles by "soft" mass spectrometric methods

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INTRODUCTION: Nanoscale, three-dimensional monolayers are mapped by generating and analysing specific surface species by mass spectrometry. New insights into the structure of the gold-thiolate interface are described.

METHODS: Thiolate monolayer-protected gold nanoparticle samples were synthesized as described previously.[1] Generally, chloroauric acid in an alcoholic solution was reduced by sodium borohydride in the presence of a homogeneous or heterogeneous thiolate ligand mixture, generating nanoparticles with a core diameter between 2-4 nm. In the case of a homogeneous ligand synthesis, the monolayer was heterogenized by the addition of a second thiolate ligand in varying amounts.

The mixed-ligand nanoparticles were analysed by matrix-assisted laser desorption/ionization-ion mobility-mass spectrometry (Synapt G2, Waters Corp.). The ion mobility separation sector is theoretically unnecessary, but has been observed to enhance signal-to-noise in collected spectra. Spectra are analysed using a custom-built spreadsheet. Specific sets of identified peaks are compared to a binomial probability distribution function model, allowing analysis of phase segregation in the heterogeneous monolayers.

RESULTS: Analysis of spectra from mixed-ligand monolayers reveals interesting transitions in fragment structure based on ligand identity. Gold-thiolate (Au-L) complexes desorbed from the nanoparticle core contain greater or fewer constituent parts (that is, numbers of Au and L) based on the identity of the ligands in the analysed monolayer (Fig. 1). This may reflect changes in binding modes or packing orientations driven by changes in ligand-ligand interaction forces. This transition has been observed by other techniques on two-dimensional surfaces,[2] but has not been explored on three-dimensional surfaces until now.

In addition, previous analyses[1] have been refined to yield a more accurate view of heterogeneous monolayers on gold nanoparticles. The new analyses suggest a strong thermodynamic role in producing observed arrangements of ligands in the monolayer.

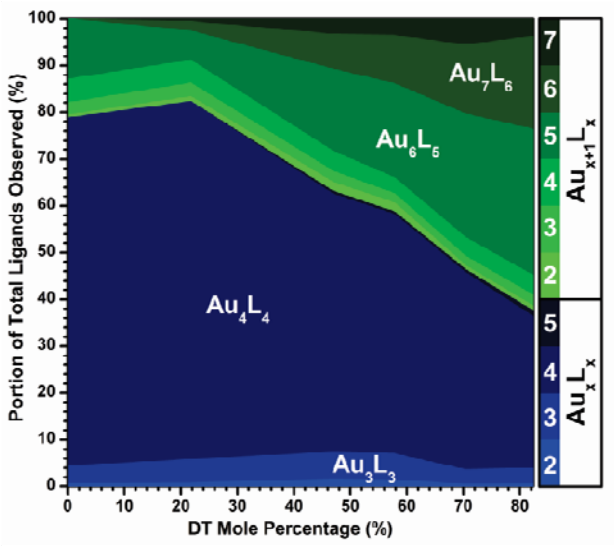

Fig. 1: The proportion of gold-thiolate complex fragments observed from a nanoparticle sample with a mixture of octanethiol (OT) and decanethiol (DT) ligands in various . As the amount of decanethiol in the monolayer increases, larger Au-L complexes become more abundant, while smaller complexes become less abundant. This transition coincides with known shifts in binding modes in alkanethiol monolayers on gold.[2]

DISCUSSION & CONCLUSIONS: These results suggest routes to new and promising areas of research, specifically the use of mass spectrometry to probe basic questions of thermodynamics and binding modes within thiolate monolayers on gold. This also affirms a growing body of work using "soft" mass spectrometry methods for interfacial and surface science. For gold-thiol model systems, an active area of research for decades, there are still a number of questions that can be answered with the right techniques.

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A MESOSCOPIC MODEL FOR C-S-H HYDRATION AND SETTING

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INTRODUCTION: Calcium-silicate-hydrate (C-S-H) is the primary hydration product of Portland cement. It precipitates and solidifies into a nano-scale gel, which literally glues together the different parts of cement and it is responsible for its mechanics. To investigate the connection between the evolution of the C-S-H gel microstructure and its rheological properties, we use mesoscale model, whose fundamental units are nano-scale particles. Although this approach does not account for the atomistic details of the C-S-H these ultimately determine the cohesive effective interaction of the nano-particles. We follow the nano-particles trajectories with Molecular Dynamics. A very important effect in the evolution of the C-S-H gel is the continuous hydration reaction. To incorporate in our model the formation of new C-S-H hydrates, we introduce Monte Carlo events of addition and deletion. The competition between effective interactions and particle formation allows cooperative motions and rearrangements, which lead to complex spatial configurations and rheological behavior.

DISCUSSION & RESULTS: We present the simulation results for two different interaction potentials that would correspond to different lime concentrations. We analyze the aggregation process for different precipitation parameters that produce different non-equilibrium structures and dynamics. Analyzing the trajectories of the MD simulations, we characterize the microscopic structure and dynamics of the gels in terms of the radial distribution function, the structure factor, the mean square displacement and the intermediate scattering function. Performing shear deformation tests by means of non-equilibrium MD, we observe different solid-like behaviors arising during far from equilibrium aggregation.

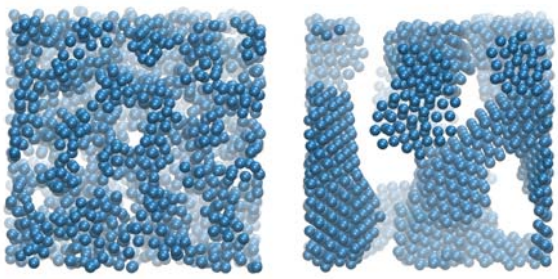

Fig. 1: Microstructures of the mesoscale gel model for C-S-H, at density ρ=0.25 and temperature T=0.3, for two different effective interactions in equilibrium.

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[4] A. Nonat, Cem. and Concr. Res., 34, 1521-1528 (2004).

[5] R.J.-M. Pellenq, A. Kushima, R. Shahsavari, K.J. Van Vliet, M.J. Buehler, S. Yip, F.-J. Ulm, PNAS 106, 16102-16107 (2009).□

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DNA translocation in Microslits

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1. DNA as a polymer

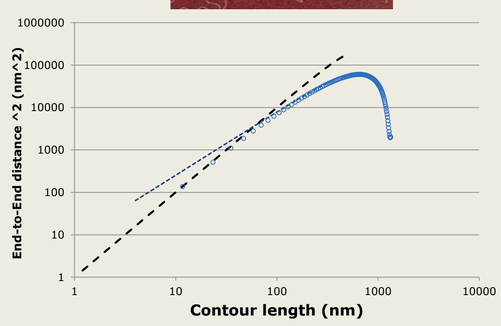
- **Elastic properties**
- **Topological properties**
- **Statistical properties**
- **Theoretical models**

$< R^2(s) > \sim A \cdot s^{2\nu}$

$< \cos\theta(s) > exp^{(-\frac{s}{2*lp})}$

lp - persistence length
v - critical exponent
R - end-to-end distance
s - contour length

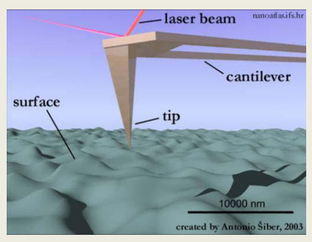
- ☑ Imaging of DNA by Atomic Force Microscopy
- ☑ Tracing the DNA molecules
- ☑ Statistical Properties in 2D:
  - ☑ End-to-End Distance
  - ☑ Correlation Function
  - ☑ Distributions



2. Why confined space and why AFM?

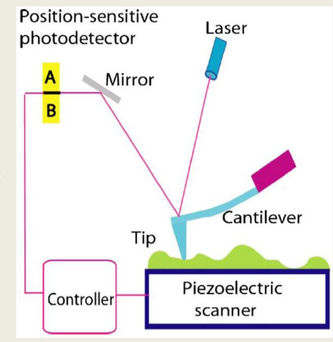
Why confined space ? - Understanding the properties of DNA in confined environments (slits in our case) is essential for the design of single-molecule analysis and manipulation devices, as well as for having a better insight in biological processes such as DNA packaging in viruses, DNA segregation in bacteria, etc.

Why AFM ? – Atomic Force Microscope is a powerful tool that provides a 3D profile of a sample surface with a nanometer resolutions, by measuring forces between a sharp probe (<10 nm) and surface at distances typically ~0.5-10 nm.



In AFM a sharp probe scans the sample surface, the position of the probe relative to the sample is controlled by a piezoelectric scanner and the vertical position of the probe is measured by a laser beam that is focused on the back of the cantilever and reflected to the photodetector.

AFM has several advantages over other techniques with equal resolution, e.g. AFM samples don't need staining, very low material amount (ng/µl) is sufficient for imaging, samples can be imaged under liquid environment, etc.

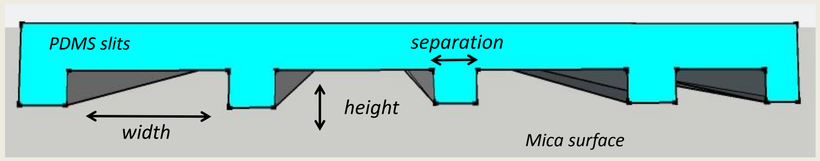


Why nanoslits? - Recent progress in manufacturing of nanodevices with defined geometries has given the ability to study statistical properties of single molecules under confined space. In our experiments we use PDMS slits to confine the DNA in one dimension , along the z axis.

3. Materials and methods

Experimental procedure

1. *Deposit slits on Mica surface*
2. *Diffuse DNA in slits*
3. *Fix DNA on the mica surface with Mg+*
4. *Remove slits and dry surface*
5. *Image with AFM & analyse the data*



2 PDMS slits :

Small slits :
width - 0.9 µm
height - 0.2 µm
separation - 0.6 µm

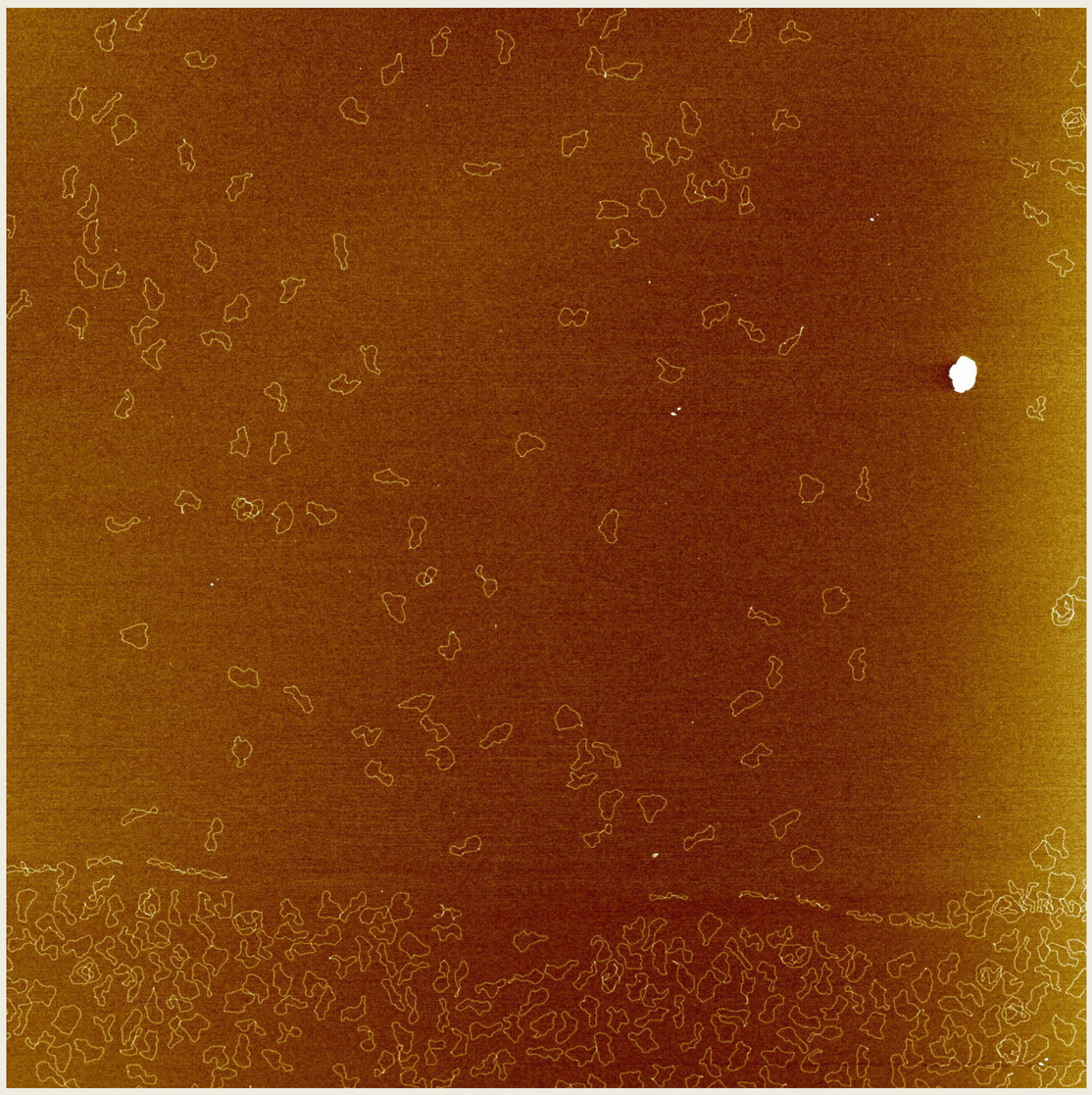
Giant slits :
width - 10 µm
height - 1.5 µm
separation - 0.6 µm

DNA Plasmids:

Puc19 (2.7kb),
PBR322 (4.4 kb),
Fx174 (5.4kb)

(Concentrations ~1ng/µl)

4. PUC plasmid 2,7kb (Giant slits)

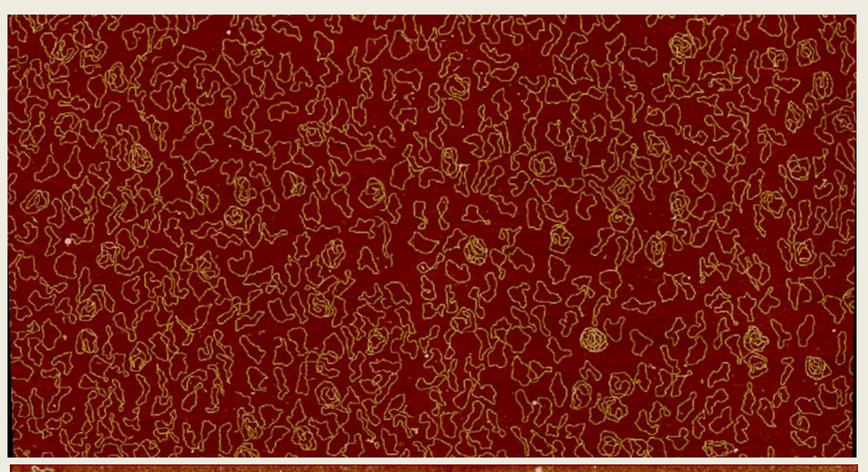


10x10µm

5. Giant vs Small slits

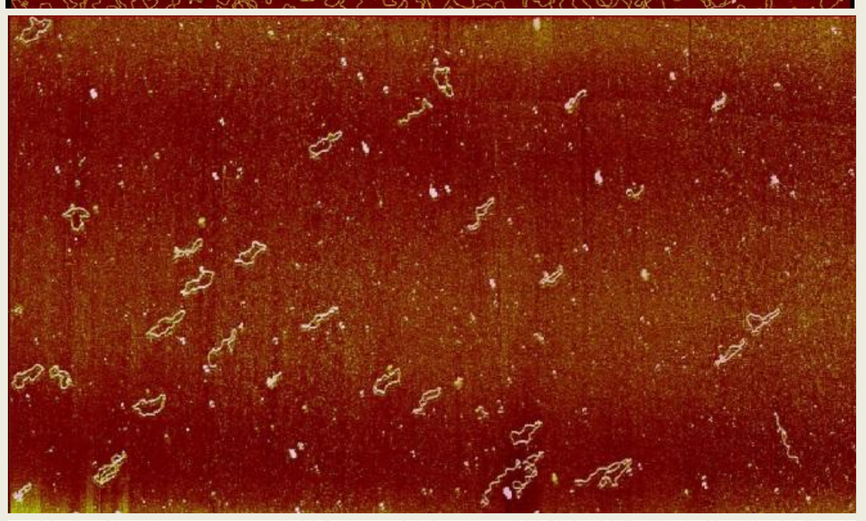
PBR plasmid 4.4kb

No slits



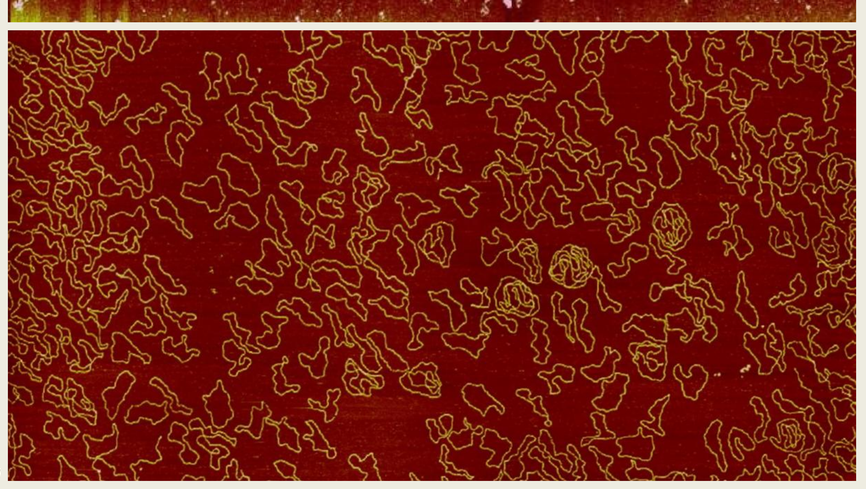
4x9µm

Small slits



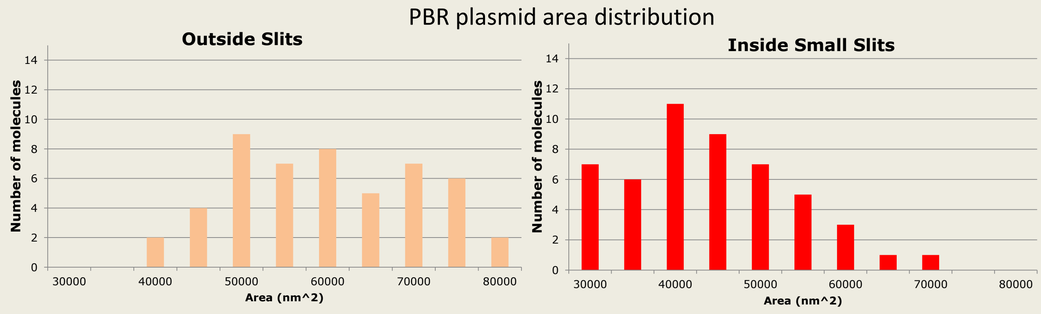
7x14µm

Giant slits



4x8µm

PBR plasmid area distribution



PBR					
Place	**Contour length (nm)**	**N**	**L_p (nm)**	**v**	**Plasmid Area (nm^2)**
No Slits	1400±40	50	51±2	0.81±0.02	60000±11000
Small Slits	1160±110	50	53±2	0.88±0.02	43500±10000
Giant Slits	1340±40	50	52±2	0.82±0.02	55000±16000

Conclusion

By combining microfluidics device with Atomic Force Microscopy technique we were able to directly visualize and measure the effect of confining space (in z dimension) on the shape and statistical parameters of circular DNA.

Our approach can be used to study the effects of various confinements and geometries on DNA molecules of different length and topology (linear, nicked and supercoiled plasmids).

Poly (N-isopropylacrylamide-*co*-tris-nitrilotriacetic acid acrylamide) to serve for molecular recognition

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INTRODUCTION: A key challenge of life science research and protein engineering is to modify, handle, immobilize or label the proteins selectively, and reserve the specificity and the activity. Nitrilotriacetic acid (NTA) and its derivatives have been broadly used for protein purification and protein immobilization due to its selective and reversible binding with hexahistidine (His6)-tagged proteins. Recently, multivalency theory was applied and the multivalent chelators such as tris-NTA exhibit an increased binding stability with His6-tagged proteins. [1] Here, we aimed to design and synthesize novel tris-NTA functionalized polymers and use them for the recognition of His peptides and His-tagged proteins.

METHODS: poly (Nipam-*co*-trisNTAam)s (PNT) were synthesized by free radical polymerization. NMR and GPC were carried out to characterise functional polymers. The chelation of Cu to the polymers was investigated by FT-IR, UV-vis, electron paramagnetic resonance (EPR) and isothermal titration calorimetry (ITC) at pH 7. The Cu-loaded polymers were used for the recognition of His6. Fast protein liquid chromatography (FPLC) and ITC were performed and the binding was investigated.

RESULTS: A library of poly (Nipam-*co*-trisNTAam) polymers was synthesized. ^{1}H-NMR of tris-NTA monomer, polyNipam and PNT is shown in Fig. 1. This trisNTA-functionalized polymer can chelate Cu and the chelation efficiency is from 91% to 100% depending on the trisNTA content in polymers. The binding of His6 to the Cu-loaded polymers was proved and a bind efficiency of 81% was calculated by FPLC (Fig. 2). ITC results confirmed that the stoichiometry of PNT/His6 complex was 1:1. The K_D of PMT/His6 complex agreed with the one of trisNTA/His6 complex. It signifies the combination of polymers doesn't affect the binding stability between trisNTA and His6.

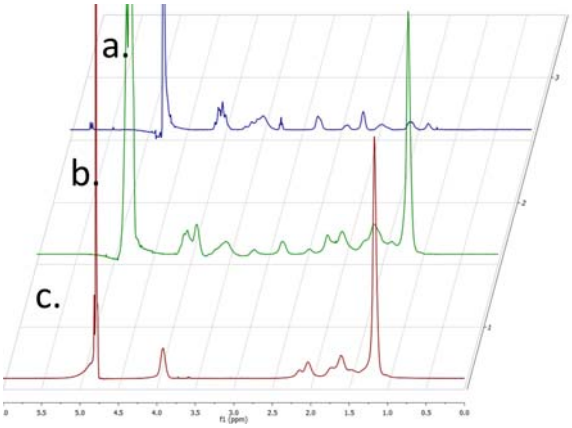

Fig. 1. ^{1}H-NMR of Tris-NTA monomer (a), poly (Nipam-co-TrisNTAam) copolymer containing 8% Tris-NTA in molar ratio (b) and polyNipam (c)

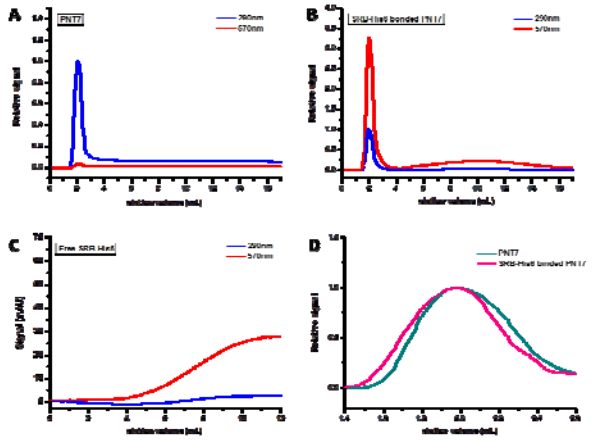

Fig. 2. (A-C) Chromatogram of PNT, PNT with 1.5-fold molar excess of SRB-His6 and free SRB-His6. (D) comparison of PNT and PNT/SRB-His6 complex.

DISCUSSION & CONCLUSIONS: A library of poly (Nipam-*co*-trisNTAam) copolymers has been synthesized and characterised. The trisNTA-functionalized polymers can efficiently bind with His6 and can be applied for medical applications.

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ACKNOWLEDGEMENTS: This work is supported by the Swiss National Science Foundation, the NCCR Nanosciences and the University of Basel. We thank China Scholarship council for the fellowship.

Controlling the Percolation in Nanoplatelets Using Polymers

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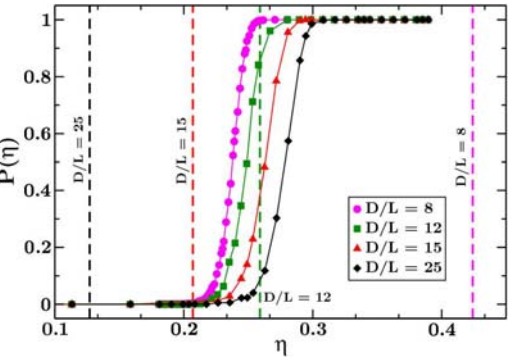
INTRODUCTION: Percolation refers to the transition of a system from containing isolated finite clusters to containing a system-spanning network that produces connectivity on a macroscopic scale[1]. This transition occurs at a specific density of the particles, called percolation threshold. Evaluation of the percolation threshold of random particle dispersions embedded in a continuous medium is an important problem in material science. For example, the formation of a percolating cluster of conducting fillers in a composite material is characterized by a sudden increase in the electrical properties of the material. It has been argued that the percolation threshold of anisotropic objects should scale as their inverse aspect ratio. This is found to be true for rodlike filler particles. However, platelike fillers are reported to disobey this principle. Using simulations, we investigate the mechanisms governing this behaviour and suggest a method to control the percolation threshold of nanoplatelets.



METHODS: We used Monte Carlo simulations for our investigation. Simulations are performed for fixed volume V and number of particles N using periodic boundary conditions. Nanoplatelets are modeled as cut spheres and polymers are modeled as spherical particles. Interactions in the system are given by the Asakura-Oosawa model, according to which hard sphere interactions are assumed between platelet-platelet and platelet-sphere pairs while sphere-sphere pairs are allowed to penetrate freely. This leads to the following pair potentials:

$u_{pp/ps}(r) = \infty$ *if overlap,* $u_{pp/ps}(r) = 0$, *otherwise*

$u_{ss}(r) = 0$.

RESULTS: Our simulations show that isotropic to nematic (IN) transition interferes with the percolation transition in nanoplatelets[2]. For larger aspect ratios, the system reaches nematic phase before percolation occurs (Fig.1). We propose that this plays a crusial role in determining the percolation behaviour of the system with respect to aspect ratio. Further, introducing spherical particles into the system results in depletion attraction between the platelets which in turn found to bring the percolation threshold to considerably lower values, a feature highly desired in real nanocomposites.

Fig. 1: interference of percolation transition with isotropic-nematic (IN) transition.

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ACKNOWLEDGEMENTS: We express our thanks to DFG for funding within the collaborative research center TR6, project D5.

Multifunctional Magnetically Responsive Alumina Microplatelets

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INTRODUCTION: 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] The surface of platelets can also be coated with superparamagnetic nanoparticles to enable 2D alignment using rotating magnetic fields.[2] Controlling the surface chemistry of reinforcing particles to enable both 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 method to coat alumina micro-platelets with a controllable layer of iron oxide nanoparticles, which can potentially be further functionalized with nitrodopamine[3] to enable deliberate tuning of the platelet surface chemistry.

METHODS: Alumina platelets, tris(acetyl-acetonato)iron(III) and benzyl alcohol were mixed in a protective nitrogen atmosphere and heated to 180°C using either a microwave or an oil bath for 30 respectively 60 min. From the black suspension obtained after heating, iron oxide coated alumina platelets could be isolated by filtration.

RESULTS AND DISCUSSION: SEM images show that a dense layer of nanoparticles covers the surface of the alumina platelets (Fig. 1(a)). The particle size can be estimated to be between 10 and 20 nm. A colour change from red to black during the reaction indicated the formation of Fe_3O_4. The platelets show a macroscopic magnetic response and can be aligned in 2D using a rotating magnetic field (Fig. 1(b)). Magnetic susceptibility measurements reveal that the coated platelets show a superparamagnetic behaviour with a saturation magnetization of about 2 emu per gram of modified platelets. We are currently investigating the composition of the iron oxide phase obtained and the potential of this simple method to tune the surface chemistry of magnetically responsive microplatelets using catechol derivatives that strongly adsorb to iron oxide surfaces.

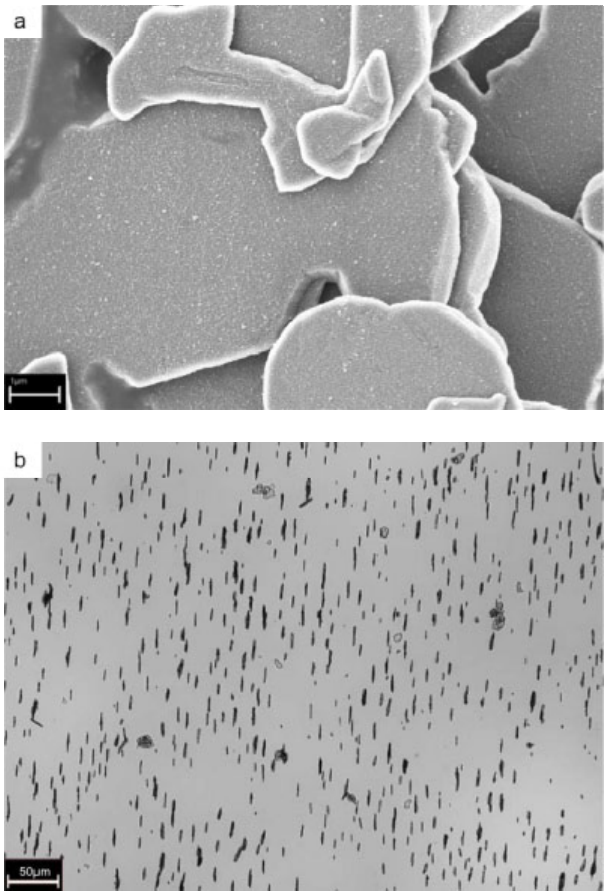

Fig. 1: (a) SEM image of alumina microplatelet covered with Fe_3O_4 nanoparticles (scale bar 1 µm); (b) magnetized microplatelets aligned in 2 dimensions by a rotating magnetic field (scale bar 50 µm).

REFERENCES: [1]T. Wang, et al. *Macromolecules* **2008**, *41*, 7656-7661. [2]R. M. Erb et.al. *Science* **2012**, *335*, 199-204. [3]E. Amstad et.al. *Small* **2009**, *5*, 1334-1342.

Minimal Model of Cell Polarization and Motion

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INTRODUCTION: Ability to migrate is a fundamental property of animal cells that underlies such important physiological and pathological processes as embryonic development, wound healing or cancer metastasis.

Directional cell motion requires polarization, i.e. development of the asymmetry of the cell shape and of the organization and activity of the cytoskeleton.

We analyze cell polarization using a model system of fish epidermal keratocytes, which are characterized by simple shape and cytoskeletal organization and regular and reproducible behavior. During early stages of polarization, zones of retraction and protrusion move along the cell edge and consolidate from several small regions to result in a nearly perfect separation of a leading (protrusive) and trailing (contractile) parts of the cell edge. Experiments suggest that local transitions of the cell edge activity from protrusion to retraction depend on myosin II and coincide with the maximum of tension between the edge and the cell body. Hence, these dynamic transitions occur preferentially at the cell extremities in both polarizing and persistently moving cells.

MODEL: These findings provide a foundation for a minimal model of cell polarization and migration based on the stochastic dynamics of protruding and retracting regions.

In the model, the cell is reduced to its edge described by a set of nodes interacting locally. Each node switches between two states, protrusion or retraction, with a transition probability depending on its neighbors and on its distance from the cell center. We investigate the parameter space of the model to determine if the polarization can develop spontaneously (that is to say without any help of external directional stimuli, from statistical edge behavior) and to analyze the resulting shapes as well as the properties of the trajectories of such motile objects. Preliminary results indicate that both persistent trajectories and asymmetrical shapes resembling those of fish epidermal keratocytes occur spontaneously at a range of model parameters.

RESULTS:

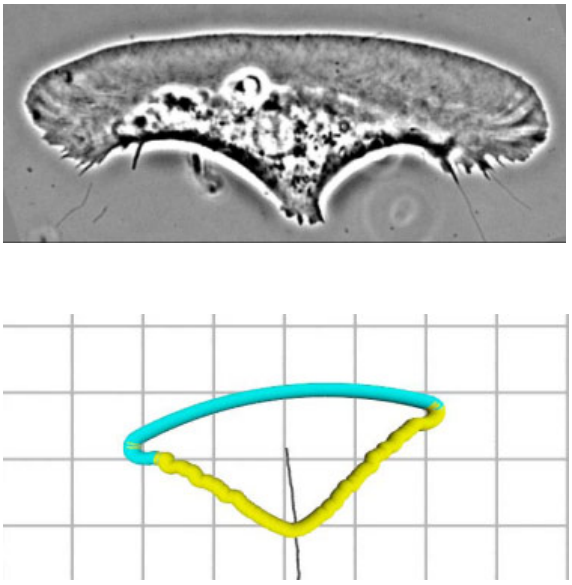

Fig. 1: Migrating fish epidermal keratocyte (top) and simulated cell (bottom). The system has 8192 nodes and the gray line indicates the trajectory of the mass center.

REFERENCES:

*High-resolution cell outline segmentation and tracking from phase-contrast microscopy images.

M. Ambühl, C. Brepsant, J.-J. Meister, A. Verkhovsky and I. F. Sbalzarini; **2012**
Journal of Microscopy, vol. 245.

*Force transmission in migrating cells.

M. F. Fournier, R. Sauser, D. Ambrosi, J.-J. Meister and A. B. Verkhovsky; **2010**

in *Journal of Cell Biology*, vol. 188.

ACKNOWLEDGEMENTS: Supported by Swiss National Competence enter for Biomedical Imaging and Swiss National Science Foundation.

Micro-Rheological Characterization of Emulsions

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INTRODUCTION:

Emulsions present a class of colloidal systems with huge commercial interest. They are omnipresent in the pharmaceutical, cosmetic and food industries. Probing their rheological properties is important to control their stability, texture and ability to be processed and spread.

Classical (mechanical) rheology is traditionally the standard technique to characterize emulsions. However, emulsions typically show effects like viscoelastic thixotropy, aging and shear banding that can lead to poor reproducibility and even artefacts when measured using mechanical rheometry.

In this study we explore the potential of microrheology based on diffusing wave spectroscopy (DWS) to access rheological properties of emulsions. This technique has several potential advantages over mechanical rheology such as the contact-free nature and the fast and reproducible data acquisition. Moreover, because the sample is not mechanically deformed, many potential artefacts like non-linear behaviour, shear banding and thixotropy can be avoided.

DWS based microrheology is able to measure the frequency dependent elastic modulus G' and viscous modulus G" as has been previously reported for several colloidal model systems [1,2]. Moreover, it has been shown that DWS can be applied to study the stability of emulsions [2,3]. However, the use of DWS based microrheology on emulsions still remains to be explored.

RESULTS:

We prepared stable oil in water emulsions with complex emulsifiers as used for body care products. The emulsions were characterized using oscillatory rheometry with cone-plate geometry (Bohlin Gemini HRnano, Malvern) and DWS based microrheology (ResearchLab, LS Instruments, Fribourg).

Fig. 1 shows that the mechanical data for G'(ω) and G"(ω) at low frequency depend on the preshear history. The overall agreement between the data from DWS and mechanical rheometry is good.

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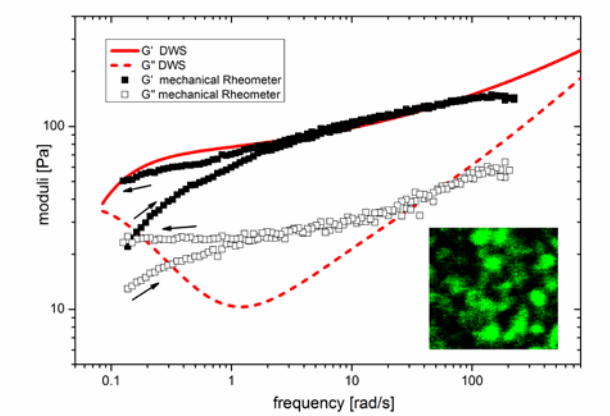

Fig. 1: Comparison of elastic modulus G' and viscous modulus G" obtained from DWS and mechanical rheometer. The arrows show the order in which the mechanical data has been measured. The inset shows a 3x3µm large confocal image from the emulsion where the droplet size can be estimated.

DISCUSSION & CONCLUSIONS:

DWS based microrheology seems ideally suited for the characterization of emulsions because of their high turbidity and low viscosity. This fast and reproducible technique has especially a high potential in monitoring stability and quality control in production chains.

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ACKNOWLEDGEMENTS: We thank Spirig Pharma AG for help with sample preparation. We gratefully acknowledge financial support from CTI project 13084.1 PFNM-NM.

Stabilization mechanism of double emulsions made by microfluidics

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INTRODUCTION: Double emulsions are used for encapsulation and release, controlled chemical synthesis or as templates for self-assembly of complex structures. Microfluidic techniques that create single and multiple droplets under well-defined flow conditions are particularly interesting, due to the high encapsulation efficiency and tight dimensional control achieved. Despite the numerous successful formulations, our understanding of the stabilization mechanisms involved at the short timescales encountered in microfluidic emulsification is still incomplete. In this work, typical effective and ineffective formulations containing both amphiphilic molecules and colloidal particles as surface active agents are investigated in detail. This systematic investigation showed that the fast formation of a strong viscoelastic particle/polymer film at the liquid interface is key for the effective stabilization of double emulsions produced in microfluidic devices.

METHODS: Monodisperse single and double emulsions were made in micro-capillary devices. The intermediate phase of the double emulsions consisted of hydrophobized silica particles suspended in toluene. Polyvinyl alcohol (PVA), PEO-PPO copolymer (PEO-PPO), PEG(20)-sorbitan monolaurate (Tween 20) or sodium dodecyl sulfate (SDS) were compared as surfactants in the continuous water phase. The effect of surfactant molecules and colloidal particles on the stability of the inner and outer droplets was investigated through designed single and double emulsion experiments. The surface activity of modified silica nanoparticles was also evaluated by measuring their individual contact angle *in situ* at the oil-water interface in the presence of different surface active species using freeze-fracture, shadow-casting (FreSCa) cryo-SEM. Interfacial rheology and pendant drop tensiometry were used to study the possible formation and rheological behavior of particle/polymer(surfactant) films at the surface of double emulsion droplets.

RESULTS & DISCUSSION: Only the polymeric surface active species PVA and PEO-PPO were found to efficiently stablilize the double emuslions droplets. Freeze-fracture SEM revealed that the nanoparticles adsorb at the toluene-water interface regardless of the surface active molecules present in the water phase, except for SDS. The nanoparticle wetting angle at the interface was similar in all cases. Despite their comparable contact angle at the toluene-water interface, the nanoparticles were found to interact more strongly with the polymers than with the surfactants present in the continuous aqueous phase. In fact, we found that such favorable interactions lead to the formation of a particle/polymer interfacial film, which is readily visible upon shrinkage of representative toluene-in-water single emulsions containing PVA (Figure 1). Interfacial rheology measurements revealed that this interfacial film is formed very rapidly, especially for PVA. The formation of an equally strong film takes much longer with surfactants in the aqueous phase or in absence of surface active species.

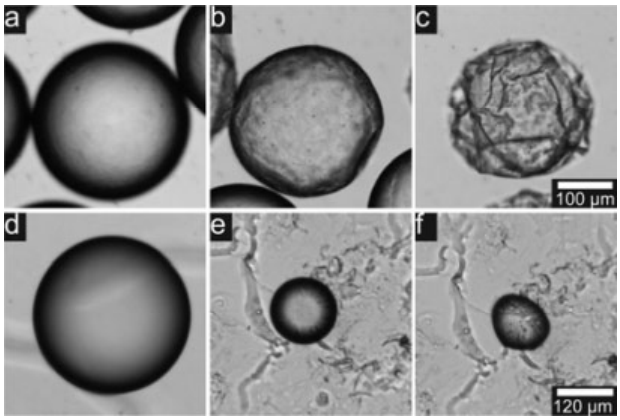

Figure 1 : Shrinkage of toluene-in-water single emulsions containing 5wt% silica nanoparticles in the oil phase and 2wt% of (a-c) PVA or (d-f) Tween 20 in the continuous aqueous phase [1].

CONCLUSIONS: Our work shows that the fast formation of a strong viscoelastic film at the oil-water interface enables the stabilization of double emulsions made in microfluidic devices. These findings provide useful guidelines for the selection of surface active species for the efficient stabilization of customized double emulsions produced with microfluidic approaches.

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Quantitative characterization of oxidized phospholipid model membranes

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We have developed a new photosensitizer agent that anchors in phospholipid membranes, limiting thus the phospholipid oxidation pathways to hydroperoxidation. We build model membrane systems, i.e.

Giant Unilamellar Vesicles (GUVs) incorporating this photosensitizer, and, using micropipette aspiration and quantitative fluorescence under optical microscopy, we show that GUVs are able to survive full hydroperoxidation. Our experimental setup allows to measure the relative area increase produced upon peroxidation (in full agreement with the fiew, recent simulation data available in literature), the associated change in mechanical properties of the membrane, and also the hydroperoxidation efficiency.

Effect of size polydispersity for nanoparticle adsorption on liquid interfaces

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Nanoparticles at liquid-liquid interfaces have stirred great interest as potential building blocks for the self-assembly of functional materials in 2 dimensions. Recent advances in the synthesis of core-shell nanoparticles with a hard core and a soft shell of grafted polymer chains offer a new material for self- assembling structures at interfaces [1].

We present numerical data investigating the adsorption of polydisperse soft shell particles towards the liquid interface. The nanoparticles are modeled via a repulsive potential which allows partial overlap of particles and represents a good compromise between numerical simplicity and the aim to model the experimental system. The motion of particles at the interface is simulated via Molecular Dynamics whereas we use a Grand Canonical Monte Carlo scheme to model the process of adsorption and desorption [2].

It is elucidated how the kinetics of the adsorption process depends upon the influx of particles and the adsorption energy. We comment on the qualititative differences and similarities in the adsorption characteristics for mono- and polydisperse size distributions of particles.

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ADSORBED AND NEAR SURFACE STRUCTURE OF IONIC LIQUIDS AT A SOLID INTERFACE

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INTRODUCTION: Ionic Liquids (ILs) are pure salts with melting points less than 100 °C. In the last years they are attracting intense research interest on account of their 'tuneability", [1,2] their often negligible vapour pressures and wide temperature and (often) redox stability ranges. There is an increasing interest regarding their structuring close to other materials surfaces due to their applicability as new batteries electrolytes.

A model for describing IL interfacial structure.[3,4] involves dividing the interface into three regions. The interfacial *innermost layer* is the layer of ions in direct contact with the surface of the other phase. This layer is often organized, and enriched in one ion or the other depending on the nature of the second material. The *transition zone* is the region over which the strong interfacial layer structure decays to the bulk morphology.

METHODS: The interfacial structure of EMI TFSI (1-Ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl) imide) on mica surface has been studied using AFM techniques in the AM-AFM mode. Several cantilevers with different force constants have been used to elucidate the structure of the different interfacial regions, always working close to resonance (typically free amplitudes of ~1nm), Each cantilever was calibrated using its thermal spectrum prior to imaging and the lever sensitivity determined using force spectroscopy. The force curves, were also obtained in the AM-AFM.

RESULTS: The external (farther from the surface) part of the IL interface has been studied using the softer levels. Progressive removal of IL layers was achieved by applying larger forces of the tip against the sample (amplitude setpoint decreasing) (Fig. 1). The amplitude vs distance force curves show the sensitivity of the system to the removal of the ordered IL interfacial layers. The inner part (closer to the surface) has been studied using the stiffer cantilevers in a similar way. Phase signal (time shifting of the tip's response) allows us to control the proximity of the tip to the surface, while RMS signal is sensitive to the presence of IL layers. Changes in the IL arrangement was observed when moving far from the mica surface, passing from a hexagonal-like distribution to a squared one due to the decreasing of the mica influence. The mica lattice can be scanned using these cantilevers, a clear signal of the penetration inside the inner part of the interfacial structure.

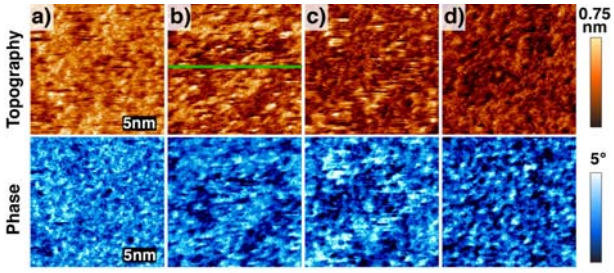

Fig. 1: Topography (up) and Phase (bottom) images of progressive removal of IL layers. Applying larger forces on the interfacial IL effectively removes the molecules.

The structuring of the EMI TFSI close to the surface shows an unexpected stability in the XY plane, while applying increasing pressure on it, originates a movement of the layer in the plane.

DISCUSSION & CONCLUSIONS: AFM techniques are useful techniques to help elucidate the structuring of IL at interfaces. The EMI TFSI structuring near mica surfaces is highly influenced by the proximity of the mica, changing from hexagonal distribution to square ones.

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Poster abstract

BULK COMPRESSION OF 2D WET FOAMS

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What is the elastic response of wet foams? An unusual characteristic of the jamming transition is the difference in scaling of the bulk and shear modulus of frictionless soft particles near jamming. Inspired by this jamming theory we probe the bulk scaling by compressing a bidisperse foam monolayer sandwiched between a glass plate and a fluid surface.

Slow relaxation in structure-forming ferrofluids

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In this work, we study strongly interacting ferrofluids by computer simulations using model parameters that mimic Cobalt-based ferrofluids used in experiments. We have investigated both, internal structures and dynamical properties of these systems for varying dipolar interaction strength. We find indications for a qualitative different structure and behavior above a critical interaction strength which is close to the estimated value for the experimental system.

Introduction:

From the classical work of de Gennes and Pincus [1], it is known that dipolar colloids having strong interactions are inclined to form chained structures. In experimental as well as numerical studies under zero field conditions [2,3,4], microstructure formation has indeed been found in these ferrofluids materials, which will strongly influence the rheological properties. In addition, some numerical studies [5, 6, 7] have also shown evidence for network formation in ferrofluids having strong dipole coupling. This has been predicted in a theoretical study by Tlusty and Safran [8].

Model :

We have used a model which has been studied previously [5, 9], where magnetically hard point dipoles are having i) a short range repulsive interaction which mimics the steric repulsion that stabilizes the ferrofluids system and ii) a long range dipole-dipole interaction. We have performed Langevin dynamics simulations in a system of 1000 dipolar particles using translational and rotational Langevin equations of motion.

Results and discussion:

We summarise our results as follows:

We have used our simulations in order to extract model parameters that reproduce the magnetisation curve of Cobalt-based ferrofluids which is shown in a recent study by Gerth-Noritzsch *et al* [10]

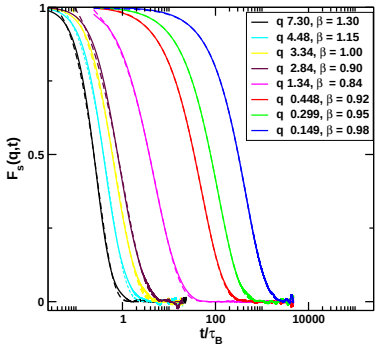

Figure 1: Self part of intermediate scattering function of $\lambda = 4.62$ shows the fast relaxation at large wave-vectors and slow relaxation in the small wave-vectors which is a characteristic feature of gel forming systems.

We have also studied the structural and dynamical properties of dipolar systems and compare the properties of systems having different dipolar strength. The static structure factor ($S(q)$) of strongly coupled system shows a peak in low wave-vectors, which is the indication of large scale structures of complex shape. The cluster size distribution, which deviates from the predicted exponential behaviour,

develops tails - reminiscent of percolating system but without clear power-law regime.

From the self-part of the incoherent scattering function ($F_s(q,t)$), we find that the system relaxes quickly at wave-vectors corresponding to the first peak of $S(q)$.The exponent from Kohlrausch-Williams-Watts (KWW) fit to $F_s(q,t)$ is greater than 1, which indicates the fast relaxation of local structures. But at small wave-vectors, we find that $F_s(q,t)$ is following a stretched exponential decay behaviour , this slow relaxation at large length scale is a characteristic feature of gel formers [11, 12].

Acknowledgments

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When attractions meet repulsions

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Many functional properties of food and other soft materials originate from the internal structuring of colloidal ingredients. Evidently, one needs glue or stickiness to hold the whole structure together. However, attractions, once introduced, tend to continue to drive the colloidal components to aggregate, rendering the structure, and thus the product, unstable. The balancing power of additional repulsions has led to development of well-defined protein aggregates and has been suggested to enable an equilibrium route to gelation. We've now designed a model system to study the phase behavior of purely attractive colloids with increasingly long-ranged repulsions. We'll present our results in the framework of the Extended Law of Corresponding States and attempt to draw a universal phase diagram of colloids interacting *via* short-range attractions and variably ranged repulsions.

Effect of amine content on PEG-Chitosan Bombix Mori nanoparticles and their uptake behaviour of bioactive molecules

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INTRODUCTION: The development of very sensitive compounds for diagnostics (contrast agents, magnetic probes) to produce new biological active systems with an improve activities to decrease doses and combined diagnostics and therapeutics for theragnostic approaches is one of the major challenges that confront nanoscience in medicine today. Based on that, combining biological molecules and synthetic nanocarriers, such as polymer supramolecular assemblies, represents a very promising strategy. Here, we present biodegradable nanocarriers based on chitosan Bombyx mori (ChsBM) and polyethylene glycol (PEG) that have been synthesized by graft polymerization with different amine content on Chitosan moieties to serve as carriers for bio-active molecules, such as antimicrobials, DNA, enzymes.

METHODS: We used ChsBM with CDA (degree of deacetylation) ranging from 88 to 96%, and molecular mass ranging from 150 to 420 kDa. Monofunctional monomethyl ether (MPEG), with a molecular mass 2000, served to avoid a cross linking reaction during of grafting process. Structures and properties of Chs-PEG copolymers have been characterized by FTIR, ^{1}H-NMR, GPS, SLS/DLS, TEM, SEM and CryoTEM.. The synthesized copolymers have a lower molecular mass (4.7 to 5.9 kDa) than the initial Chs chains, a low polydispersity, and a degree of substitution ranging from 40 to 100 %. The low molecular mass indicates a partial destruction of chitosan domain during the copolymerization. Due to the different molecular mass and CDA, different batches with an amine content range between 1.1-0.7 % were obtained.

RESULTS: Based on the hydrophilic to hydrophobic ratio, ChsBM-PEG copolymers self-assembled in dilute aqueous solutions, and generated supramolecular assemblies. Spherical objects, with sizes around 200-250 nm, have been observed by TEM and CryoTEM (see Fig 1), and characterized by static and dynamic light scattering. Their size has been modulated by the density of the hydrophobic domain. Hydrophobic and hydrophilic molecules were used for the uptake behavior. The results show entrapment of the hydrophobic dye for all the nanoparticles reported in this work but only entrapment of the hydrophilic dye for the nanoparticles with low amine content. FCS measurements show a typical shift on the correlation function (from free hydrophobic free dye τ_D = 56 μs to free dye-ChsBM-*O*-PEG τ_D = 999 μs and hydrophilic free dye τ_D = 54 μs to free dye-ChsBM-*O*-PEG τ_D = 2239 μs). This hydrophilic entrapment is only observed for spherical objects with less amine content (ChBM-*O*-PEG; N_{NH2} 0.7 %).

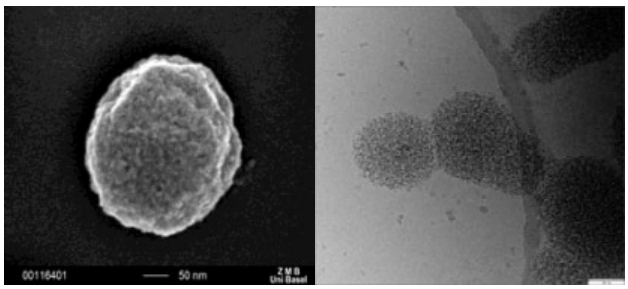

Fig. 1: SEM micrograph of ChsBM-PEG nanocarrier (left) Cryo-TEM micrograph of ChsBM-PEG nanocarrier (right).

DISCUSSION & CONCLUSIONS: The modification of chitosan with a hydrophilic domain serves to induce an amphiphilic character of the resulted copolymers, which will favor the self-assembly process generating supramolecular assemblies. The self-assembly process generating nanocarriers allows a mild entrapment procedure, ideal for sensitive antimicrobial/enzymes. The results show that the entrapment depends on the amine content on chitosan moieties. The smart combination of stability (stable for more than three weeks), and biodegradability in biological conditions, make these novel ChsBM-PEG nanocarriers to be ideal for the transport of sensitive biological molecules, and thus to serve for an efficient approach in food applications.

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The self-assembly phase diagram of PDMS-PMOXA diblock copolymer

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INTRODUCTION: Both poly (dimethylsiloxane) (PDMS), and poly (2-methyl-2-oxazoline) (PMOXA) have been used in various technological and medical applications, such as surface engineering and biomaterials due to their intrinsic properties.[1,2] PMOXA-PDMS-PMOXA triblock copolymers self-assemble in vesicles, whose membrane allowed insertion of various channel proteins, such as Ompf.[3] A step further in simplifying the system is to synthesize PDMS-PMOXA diblock copolymers, and investigate their self-assembly behavior for further applications. Here we present the development of a PDMS-PMOXA diblock copolymers library with various hydrophobic to hydrophilic ratio and their self-assembly behavior.

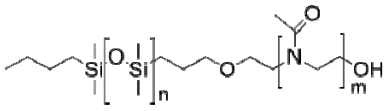
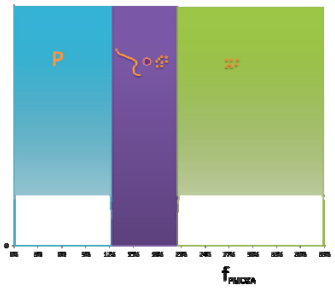


Fig. 1: The chemical structure of PDMS-PMOXA diblock copolymer.

METHODS: The self-assembly morphologies are obtained by the film rehydration method with polymer concentration 5 mg/ml at room temperature. The self-assembly morphologies are characterized by transmission electron microscopy and static and dynamic light scattering.

RESULTS: The phase diagram of two sets of copolymers has been obtained. Each phase diagram contains the self-assembly behaviour of diblock copolymers with the same PDMS block length, and with different PMOXA block lengths. Depending on the hydrophobic-to-hydrophilic ratio, there are distinct domains of self-assembly behaviour: formation of micelles, formation of vesicles, or mixture of these architectures.



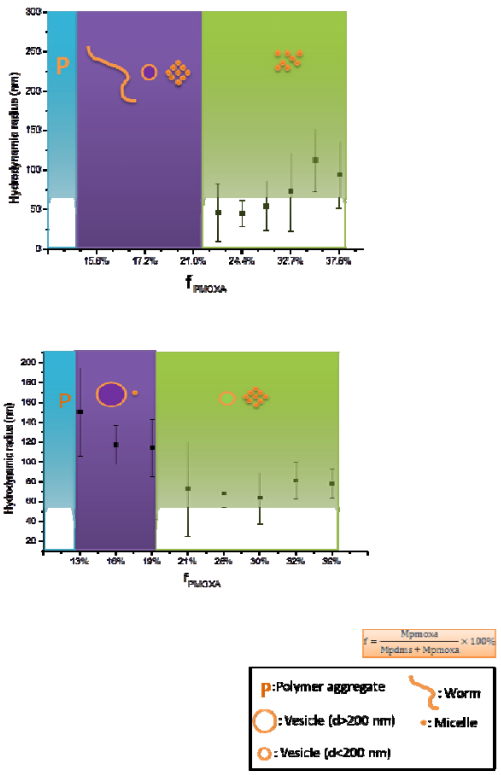


Fig. 2: The phase diagram with molecule weight of PDMS 1.4kDa (upper); the phase diagram with molecule weight of PDMS 3.1kDa (middle); the phase diagram with molecule weight of PDMS 5.0kDa (lower).

DISCUSSION & CONCLUSIONS: A library of PDMS-PMOXA diblock polymers was successfully synthesized through cationic ring-opening polymerization. The phase diagrams clearly indicates the effect of diblock copolymer molecular properties on their self-assembly behavior.

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STUDIES OF AMPHIPHILES CONTAINING AN AMIDE, UREA OR THIOUREA INTERFACE

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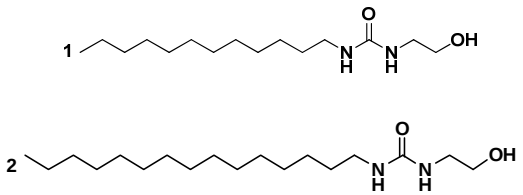
INTRODUCTION: Acyl ethanolamines (NAEs) are naturally occurring single-chain amphiphiles with different medical applications (analgesic, antibacterial, anti-inflammatory).[1] The biophysical properties of the NAEs are equally interesting showing a high propensity to form bilayer-type structures with strong inter-hydroxy group hydrogen-bonding networks and equally strong inter-molecular amide N-H to C=O hydrogen bonds.[2] NAEs would serve as readily accessible model compounds for studying intermolecular forces found in more complex phospholipid systems.[3] Here, we set out to explore the effects of exchanging the amido units with urea and thiourea moieties.

RESULTS:

The urea **1** and **2** (Fig. 1), their thiourea analogs and the amide analog of **2** (the analog of **1** was already prepared and studied in an earlier report[4]) were synthesized and characterized.

Fig.1: C14 and C17 urea amphiphiles studied.



The melting points of all compounds were measured (see Table 1 for **2** and its derivatives). One would expect to see a large influence of the hydrogen-bonding motive. Clearly, the ureas were showing the highest melting points. The corresponding amides were melting 10 °C earlier and the thioureas were melting another 20 °C lower. As the hydrophobic portions of the molecules did not change, the main driving force for the difference in melting temperatures must come from the chemical moiety at the interface.

*Table 1. Comparison of the melting points of the urea **2** and its amide and thiourea analogs.*

	Melting point [°C]
Thiourea	75-77
Amide	99-101
Urea	112-113

Next, surface pressure/molecular area isotherms (π-A isotherms) were recorded. The surface pressure/molecular area isotherms showed no temperature or chain-length dependence for the ureas. Thioureas or amides do show a clear dependence of monolayer organization and tail length. For thioureas a balance between the forces in the tails (van der Waals) and the forces in the headgroups (zig-zag hydrogen-bonding network) were found. Similarly, an increase in the temperature led to a decrease of the molecular packing order of amide and thiourea.

DISCUSSION & CONCLUSIONS: By investigating acyl ethanolamide analogs, the long-tail urea ethanolamines showed the highest degree of organization, the thiourea ethanolamines the lowest, with a temperature and chain-length dependent medium organization.

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Probing Membrane Proteins Incorporation into A Biomimetic Solid-supported Polymer Bilayer

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Biomimetic membranes with incorporation of membrane proteins have prospective technological applications, such as drug screening, trace analysis and biosensor. Amphiphilic block copolymers are promising candidate as artificial membrane matrix. Solid supported membranes, especially tethered solid supported bilayer membrane (TSSBM) that attaches the membrane onto a planar solid surface by a chemical or a physical bond, are more promising for prospective technological applications because of the resulting mechanic stability. By consecutive Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) transfers, homogeneous and defect-free amphiphilic poly(butadiene)-block-poly(ethylene oxide) (PB-PEO) TSSBM was served as a suitable platform to probe the biomimetic potential of TSSBM for membrane protein incorporation. We will present our recent work on reconstitution of membrane proteins, α-haemolysin (αHL) and out membrane protein F (OmpF)), into this polymer TSSBM. It was proved that functional incorporation of membrane proteins can be achieved in completely artificial block copolymer TSSBM by electrical conductance measurement and AFM scanning. A special electrical conductance change during channel protein reconstitution into TSSBM was observed. Mechanism for the special conductance change during membrane protein incorporation was discussed.

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