Swiss Soft Days

10th Edition
Paul Scherrer Institut

Monday, March 4th 2013

Program
&
Abstracts

Swiss Soft Days X

4. March 2013, 10:00 to 17:30

Paul Scherrer Institut, Villigen – PSI West, Auditorium

10:00-10:20	Registration and coffee	
10:20-10:30	*Kohlbrecher (PSI)*	Welcome

Session I – Biological Systems

10:30-10:50	*Axel Hochstetter (U. Basel)*	Power of Parasites – Chemical influence on Trypanosoma motility
10:50-11:10	*Giovanni Longo (EPFL Lausanne)*	Rapid Evaluation of Bacterial Antibiotic Resistance
11:10-11:30	*Gergely Nagy (PSI)*	Light-induced reorganizations in the thylakoid membrane ultrastructure of higher plants and algal cells
11:30-11:50	*Claudiane Ouellet-Plamondon (ETH Zürich)*	Thermal and Wetting behavior of Nanocellulose and genetically engineered fusion protein
11:50-12:05	Coffee	

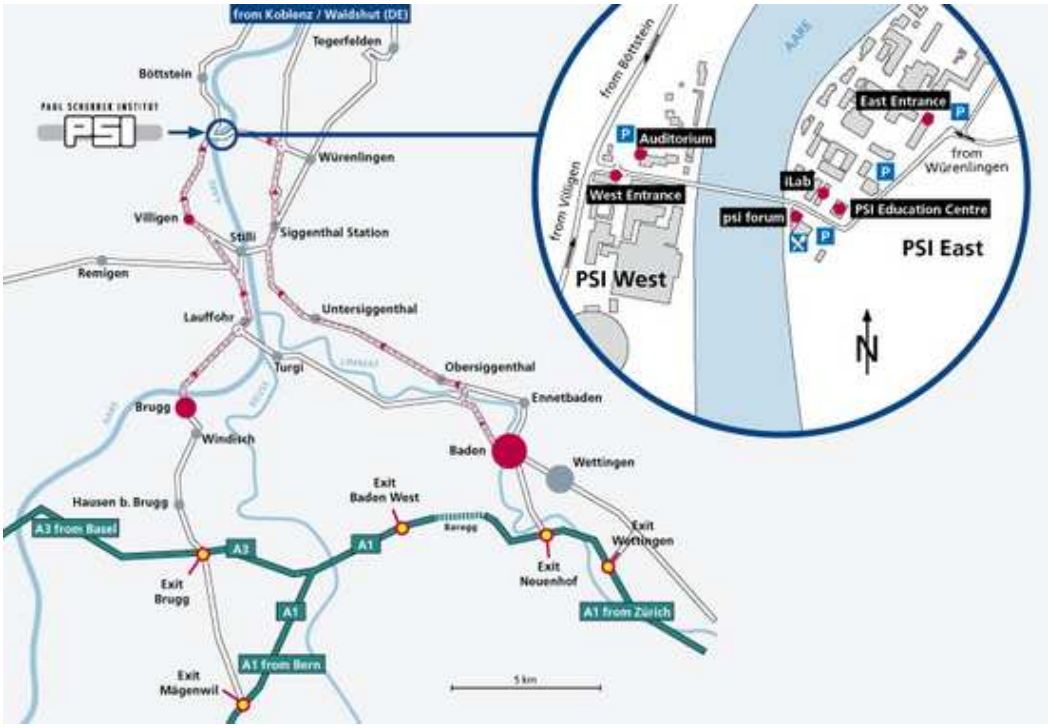
Session II – Methods

12:05-12:25	*Nico Bruns (U. Basel)*	Fluorescent protein senses and reports mechanical damage in fiber-reinforced polymer composites
12:25-12:45	*Niccolò Piacentini (EPFL Lausanne)*	Ultralow spring constant SU-8 cantilevers for biophysical measurements
12:45-14:15	Lunch / Poster	

Session III – Materials and Assemblies

14:15-14:35	*Kitty van Gruijthuijsen (Firmenich & HES-SO Valais)*	When Attraction meets repulsion
14:35-14:55	*Marco Lattuada (U. Fribourg)*	Microstructure Manipulation in Porous Materials via Magnetically-controlled Phase Separation
14:55-15:15	*Simone Liuzzi (PSI)*	Ion specific effects on layering of nanoconfined salt solutions
15:15-15:30	Coffee	
15:30-15:50	*Francesco Simone Ruggeri (EPFL Lausanne)*	Study of early stage of amyloids fibrils formation in α-synuclein by AFM Single Molecule Statistical Analysis
15:50-16:10	*Sophia Jordens (ETH Zürich)*	Non-equilibrium nature of 2D isotropic and nematic coexistence in amyloid fibrils at liquid interfaces
16:10-16:40	*Konrad Schwenke (ETH Zürich)*	Collective processes in the adsorption of nanoparticles at liquid-liquid interfaces
16:40-17:40	Poster Session	
17:40-17:50	*Kohlbrecher (PSI)*	Closing Remarks
17:50	Wrap-up with beer, wine and snacks	

How to get to the Paul Scherrer Institute?



Direction to PSI Download
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PSI is located in northern Switzerland, approximately midway between Zürich and Basel. The nearest towns and railway stations are Baden and Brugg. Frequent air and train connections via Zürich or Basel are available from all major European cities.

To find PSI by car

You can reach PSI via Brugg or Baden.

Via Brugg:
Follow the Koblenz–Zurzach signs through Brugg. After passing through Lauffohr and a short hill, branch off to the left towards Remigen/Villigen; then after about 500 m turn right towards Villigen. Approximately 1 km after leaving Villigen you will reach PSI-West. You can drive to PSI-East via the bridge over the river Aare.

Via Baden:
Follow the Koblenz–Zurzach signs through Baden. Drive through Nussbaumen, Untersiggenthal and Station Siggenthal. Approximately 1.5 km beyond the roundabout, follow the sign left towards PSI at the crossroads and you will reach PSI-East. You can drive to PSI-West via the bridge over the river Aare.

Programming of the navigation system:
For PSI West: enter city "Villigen", street "PSI"
It is permitted to use the connecting road across the river Aare.

To reach PSI by public transport

Brugg is on the train line (Zürich–Basel, Zürich–Bern). You can take a public bus (Postauto) from Brugg railway station. Take the Brugg–PSI–Böttstein–Döttingen bus, and within 20 minutes you will arrive at PSI.

Abstractd for the talks

Power of Parasites – Chemical influence on *Trypanosoma* motility

Axel Hochstetter[1], Eric Stellamanns[2], Sravanti Uppaluri[2], Niko Heddergott[3], Markus Engstler[3], Thomas Pfohl[1,2]

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The motility of unicellular parasites in mammalians is very fascinating, yet very complex. In a world, where inertia cannot be used for propulsion, in a world at low Reynolds numbers, most of our everyday's macroscopic strategies of self-propulsion do not work.

One class of parasites that know their way around, the flagellate *Trypansome,* manage to navigate in the blood stream, which flows a lot faster than the *Trypanosome's* own propulsion velocity. There, the *Trypanosomes* are constantly attacked by its host's immune response. Yet, they survive and even penetrate the blood-brain-barrier, which actually should be too tight to enter. Although *Trypanosomes* are known for more than 100 years, their motility strategies and switching of motility modes are not completely elucidated yet.

Using high-speed microscopy in combination with optical tweezers in microfluidic devices and analyzing the recorded data, new light has been shed on the motility of these parasites.

Our results show that *Trypanosomes* can be optically trapped, and dragged through microfluidic devices without harming them. Once caught in an optical trap, they rotate in elaborate patterns. By analyzing the power-spectrum for our high-speed image-series we have discovered two main rotation frequencies.

Furthermore we probe the impact of their chemical environment and of objects in close proximity, such as particles, red blood cells and other *Trypanosomes,* by analyzing their motility behaviour.

Rapid Evaluation of Bacterial Antibiotic Resistance

G. Longo, L. Alonso-Sarduy, J. Pekkanen, G. Dietler, S. Kasas.
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Antibiotics represent one of humanity's most important medical inventions, yet antibiotic resistance has emerged as a very significant health care problem due to the extensive use and misuse of antibiotics in human and veterinary medicine. Suppressing the emergence and propagation of antibiotic-resistant bacteria is one of the major health issues of the present century.

To deliver a complete antibiogram, conventional techniques require, for most bacterial strains, more than 1 day and several days or weeks in the case of slow-growing microorganisms. We present a new nanomechanical oscillator system capable of detecting movement of biological samples (from proteins to bacteria or cells) at the nanoscale. The technique is versatile and simple and can be applied to several systems of interest in the fields of medicine, drug-development or microbiology. This novel system is capable of quantitatively determining, in less than 30 minutes, the response to antibiotics of any bacterial strain including slow-growing microorganisms.
Such extremely fast characterizations have been exploited to study Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) strains and preliminary results will be presented of the application of this technique to study *Mycobacteria*.

The speed and sensitivity of the technique will have a massive impact, allowing drastically reducing the time needed to obtain a complete antibiogram. This will potentially change the therapy of infections caused by multi-resistant bacteria as well as the development procedures of new antibiotic drugs.

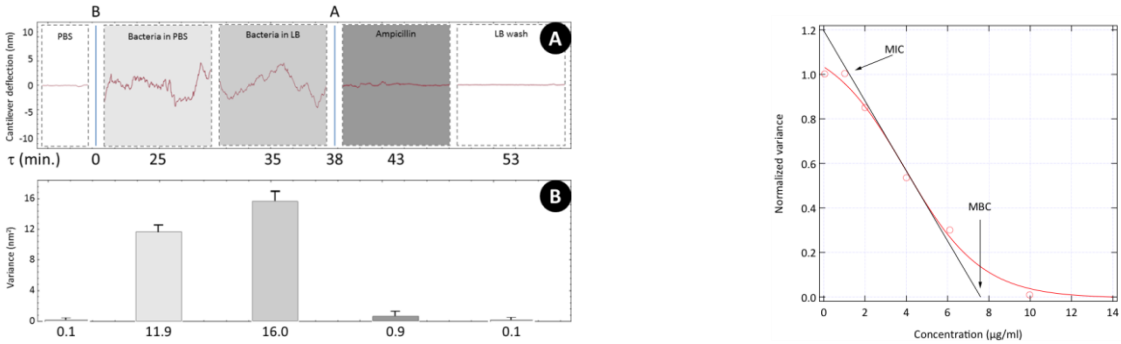

Fig 1. Proof of concept of the nanomotion sensor. Left panel: *Response of Escherichia coli to the exposure to different stimuli, including an ampicillin-rich medium.* ***Right panel:*** *Quantitative reconstruction of a complete antibiogram using the nanomotion sensor.*

Light-induced reorganizations in the thylakoid membrane ultrastructure of higher plants and algal cells

G.Nagy[1], L.Kovács[2], R.Ünnep[3], O.Zsiros[2], M.Szabó[4], L.Porcar[5], L.Rosta[3], J.Minagawa[6], G.Finazzi[7], J.Peters[5,8,9], P.Timmins[5], D.Posselt[10], G.Garab[2]

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INTRODUCTION: Thylakoid membranes play central role in photosynthesis of cyanobacteria, algae and plants, by giving place to virtually all the light reactions. In our works we investigated the thylakoid membranes with small angle neutron scattering, which is capable of providing statistically averaged repeat distance values for multilamellar biological membranes on samples without staining and fixation, under physiologically relevant experimental conditions.

METHODS: Small angle neutron scattering measurements were performed on suspensions of isolated thylakoid membranes or of entire algal cells placed in temperature controlled quartz cuvettes. In situ illumination was performed with a light guide. In order to increase the signal-to-noise ratio, magnetic field, perpendicular to the neutron beam could also be applied.

RESULTS: We determined the characteristic repeat distances and revealed light-induced structural reorganizations during photosynthesis in thylakoid membranes isolated from higher plants and in different algal and cyanobacterial cells *in vivo* [1-3], with a time resolution of seconds and minutes [4]. We could correlate the measured repeat distances with the macro-organization of the different photosynthetic complexes. We also provided experimental evidence for changes in thylakoid membrane stacking in green algae during state transitions.

Our results reveal unexpectedly high structural flexibilities of these multilamellar membrane systems and provide clear evidence for the occurrence of small but well discernible thylakoid membrane reorganizations during illumination, which can be associated with special functional activities during photosynthesis.

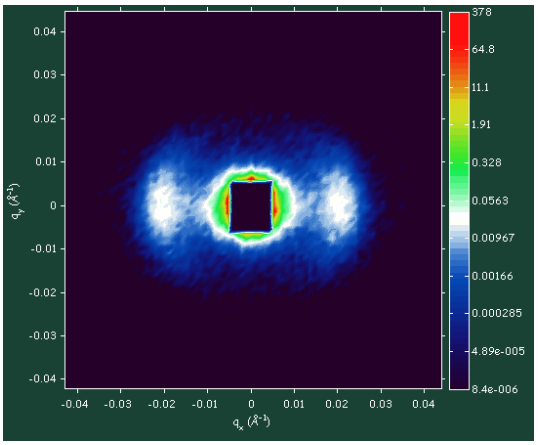

Fig. 1: Two-dimensional SANS profile of magnetically oriented spinach thylakoid membranes, recorded with the D22 SANS instrument (ILL)

DISCUSSION & CONCLUSIONS: These studies, apart from answering questions about the structure of these photosynthetic membranes, also demonstrate the power of neutron scattering for the study of complex biological systems.

REFERENCES: [1] G. Nagy; **2011**; *Biochem J;* 436:225-230., [2] G. Nagy; **2012**; *Photosynth Res;* 111:71-79. [3] D. Posselt; **2012**; *Biochim Biophys Acta Bioenerg;* 1817:1220-1228. [4] G. Nagy; *submitted*

ACKNOWLEDGEMENTS: We thank the Institut Laue-Langevin, the Paul Scherrer Institut and the Budapest Neutron Centre for providing us beamtime for the experiments.

THERMAL AND WETTING BEHAVIOR OF NANOCELLULOSE AND GENETICALLY ENGINEERED FUSION PROTEIN

C. Ouellet-Plamondon[1], J.-M. Malho[2], M. Linder[2], I. Burgert[1]

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INTRODUCTION: A fusion genetically engineered fusion protein (HFBI-DCBD) incorporates a hydrophobin block to bind to hydrophobic substances and a cellulose binding block[1]. We investigated the thermal and wetting behavior of this nanocellulose-protein composite.

METHODS: The samples were synthesized according to Laaksonen et al[1)]. The thermogravimetric analysis (TGA) was conducted with a TA Q50 from TA instrument. The 2.2 mg sample was placed in a platinum pan and heated 10°C/min until 1000°C in nitrogen. The derivative TG (DTG) shows the mass loss rate as a function of temperature. The ATR-FT-IR spectroscopy measurements were taken with a Perkin Elmer Spectrum 100 in the 4000 to 600 cm^{-1} range with a resolution of 4 cm^{-1} for 50 scans fitted to baseline. The moisture sorption and desorption isotherms were generated with the TA VTI-SA Vapor Sorption Analyser. The procedure was optimized to the 10%, 25%, 50% and 85% steps. The sample was initially dried at 105 °C for 60 min. Equilibrium was assumed when there was no mass change more than 0.0010% in 2 minutes with the condition that equilibrium must be reached within 360 minutes. The wetting behavior of the films was measured by a contact angle measuring device with video extensiometry OCA 20 from DataPhysics.

RESULTS: Three maxima were visible in the DTG curves (Fig. 1). The first maximum corresponds to the evaporation of the adsorbed water, while the second to depolymerization, dehydration and decomposition of the glycosyl units and the third to the formation of charred residue[2]. The apparent activation energies of the main pyrolysis process were determined by the Friedman and the Broido methods [2,3](Table 1).
FTIR spectroscopy showed the amid I band of protein around 1650 cm^{-1} associated with the C=O vibration, and the amid II band at 1550 cm^{-1} associated with the N-H bending vibration and the C-N stretching vibration. The moisture sorption and desorption showed that the NFC-protein adsorbed 7% more water than the NFC alone and hysteresis. The initial contact angle (CA) of the NFC-protein was higher and more stable over time than the NFC in the preliminary measurements.

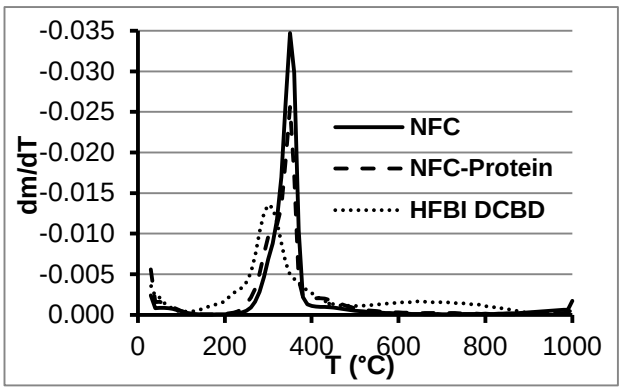


Fig. 1: Derivative thermogravimetric (DTG) curves

Table 1. Apparent activation energy calculated from TGA

	T (°C)	Ea (kJ/mol)	r^2
Friedman method			
NFC	200-350	97	0.99
NFC-Protein	200-350	68.6	0.98
Broido method			
NFC	260-350	91.9	0.97
NFC-Protein	260-350	73.9	0.99

DISCUSSION & CONCLUSIONS: A shoulder was observed in the DTG at 300°C in NFC-protein sample, which correspond to the maximum of the protein. The NFC-protein lowered the activation energy, thus acted as catalyst. It adsorbsed more water, but its surface was more hydrophobic. This work provides insight on making new nanocellulose hybrids.

REFERENCES: [1] Laaksonen et al; **2011**; *Angew. Chem. Int. Ed.;50*: 8688-8691. [2]Roman and Winter; 2004; Biomacromolecules;5(5):1671-1677. [3]Yao et al; 2008; Polym Degrad Stabil; 93(1):90-98.

ACKNOWLEDGEMENTS: Tina Kuenninger helped with the contact angle measurements.

Fluorescent protein senses and reports mechanical damage in fiber-reinforced polymer composites"

N. Bruns, Chemistry Department, University of Basel

Abstract:

Some molecules change their color or fluorescence in response to mechanical forces. When incorporated in polymeric materials, these mechanophores become useful probes that enable detection of micron scale-damage or render stress distributions visual. The fluorescence of fluorescent proteins is linked to their native structure, which can be distorted by mechanical forces. Here, we present that enhanced yellow fluorescent protein (eYFP) loses its yellow fluorescence when subjected to macroscopic forces and show the implementation of this protein as a mechanophore in a polymeric material. eYFP was used as a force-sensitive link between epoxy resin and glass-or carbon surfaces and in fiber reinforced composites. The biomolecule reports shear debonding and barely visible impact damage by loss of fluorescence. The resulting self-reporting materials could find application as a safety feature in load-bearing components to prevent catastrophic material failure.

Ultralow spring constant SU-8 cantilevers for biophysical measurements

N.Piacentini, J.-J.Meister, B.Vianay

[1] *EPF Lausanne, Lausanne, Switzerland.*

INTRODUCTION: Currently existing custom devices to apply and sense forces at the cell scale are either bulky, involving whole-cell measurements, or they require complex and expensive fabrication and detection.
In order to target subcellular applications, we propose a cheap and easy-to-fabricate force sensor with very low spring constant (down to 0.5 nN/μm) and optical readout. The device is fabricated in SU-8 photoresist, to date the most widespread polymer for lab-on-chip and micro electromechanical system fabrication [1].
This work reports on the fabrication and use of high aspect ratio and ultralow spring constant cantilevers, featuring a thickness of 5 μm, a width of 5, 10 or 20 μm, and a length of 100 – 1200 μm.

METHODS: Cantilevers are fabricated by adapting a protocol described in [2]. Double-side polished silicon wafers are first dry etched in the backside for alignment markers. Frontside is then sputter-coated with TiW/Al, and SU-8 lithography defines in two steps the devices (5-μm thick) and their supports (50 μm). Anodic dissolution of the metal sacrificial layer finally releases the structures.
The fabricated devices are first inspected by optical microscopy and profilometry, and Scanning Electron Microscopy, in order to assess their geometrical properties which determine the mechanical behaviour. Mechanical properties of the cantilevers are then evaluated with an atomic force microscope in force spectroscopy mode to assess the spring constant of the beams (Fig. 1).

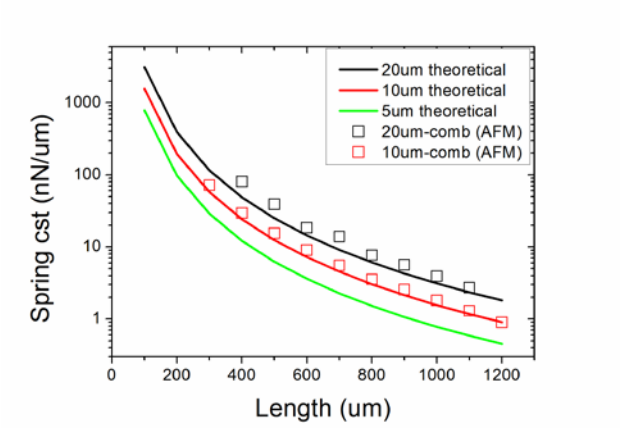


Fig. 1: Theoretical (solid curve) and experimental spring constants (squares) for the fabricated cantilevers (error bars smaller than the squares).

A SU-8 cantilever installed vertically on a micromanipulator via a custom holder is used under the microscope to approach living cells, formerly allowed to spread overnight onto adhesive protein cross pattern. Micropatterns are used to constrain the cells to adopt reproducible shapes and stress fiber organizations [3]. Cells are moved relatively to the beam by means of a motorized stage and the in-plane deflection of the cantilever is optically detected using a post-processing alignment algorithm.

RESULTS & DISCUSSION: The mechanical characterization (Fig. 1) shows that the devices meet the specifications over a wide range of spring constant, actually extending by several orders of magnitude the minimum applicable and detectable forces of commercial probes. The experiment (Fig. 2) validates the sensitivity of the cantilever and its capability of local manipulation of stress fibers.

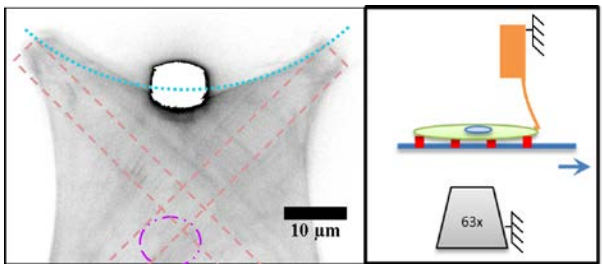


Fig. 2: A fibroblast on protein pattern (dotted cross) subjected to stress fiber compression with a 5x5x800μm cantilever (k=1.5 nN/μm). The fiber elongates from its rest position (cyan line) by 1,24% under a force of 36 nN (magenta ellipse marks cantilever rest position).

CONCLUSION: We reported about the successful design, fabrication and utilization of SU-8 polymer cantilevers, suitable for investigation at the cellular scale (width down to 5 μm, spring constant down to 0.5 nN/μm). The developed tool is capable of addressing sub-cellular structures and opens news perspectives in single cell stretching and cell-cell adhesion.

REFERENCES: [1] P. Abgrall; **2007**; *Electrophoresis;* 28:4539-4551. [2] A. Mercanzini; **2008**; *Sens Actuator A-Phys;* 143:90-96. [3]H. Guillou; **2008**; *Exp Cell Res;* 314:478-488.

ACKNOWLEDGEMENTS: EPFL-CMi and S. Jiguet for fruitful microfabrication discussions.

When attractions meet repulsions

Kitty van Gruijthuijsen
Adolphe Merkle Institute, University of Fribourg
Current : Firmenich & HES-SO Valais

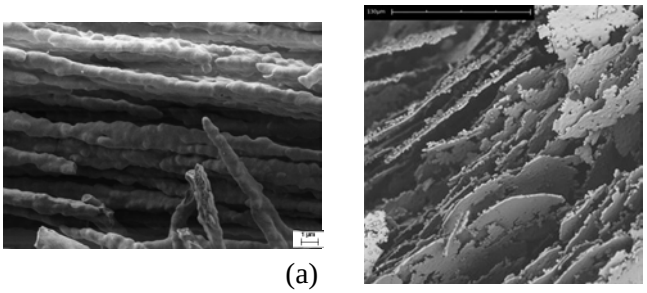
Many functional properties of food and other soft materials originate from the internal structuring of colloidal ingredients. Evidently, one needs glue or stickiness to hold the whole structure together. However, attractions, once introduced, tend to continue to drive the colloidal components to aggregate, 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.

Microstructure Manipulation in Porous Materials via Magnetically-controlled Phase Separation

M. Furlan, M. Lattuada

[1]Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland

Sol-gel accompanied by phase separation is an established method for the preparation of porous silica monoliths with well-defined macroporosity, which find applications in chromatography and catalysis. In this work, we demonstrate how the addition of (superpara)magnetic nanocolloids as templates to a system undergoing a sol-gel transition with phase separation leads to the creation of monoliths with a completely different microstructure, which can be controlled by the application of a magnetic field. It is known that magnetic nanocolloids respond to the application of a uniform external magnetic field by self-assembling into columnar structures. When the same colloids are instead exposed to a rotating magnetic field, they self-assembly into two-dimensional sheet-like structures. The application of either a static or a rotating magnetic field during the chemically-induced spinodal decomposition triggered by the sol-gel transition allows one to break the symmetry of the microstructure. The growth of silica structures reflects the self-assembled magnetic particles configuration. Therefore, magnetic elongated needle-like silica domains incorporating the magnetic nanocolloids, aligned in the direction of the field are created under static field. Conversely, platelets structures with planar symmetry are obtained in the case of rotating fields. It is found that these microstructures impart strong mechanical anisotropy to the materials. In the first case, the ratio between the Young's modulus values measured in a direction parallel and perpendicular to field can be as high as 150, with an overall smaller average macropores size as compared to isotropic monoliths. In the second case, the materials are one order of magnitude more resistant in the plane where the rotating field was applied than in the perpendicular direction. The microstructure and properties of the porous monoliths can be further controlled by changing both the system composition and the strength of the applied magnetic field. Additionally, more complex structures can be prepared by non-uniform fields, magnetic field gradients, or alternating fields. Our monoliths represent the first example of materials prepared by magnetically controlling a phase transition.



(a) (b)

Figure 1 SEM picture showing the microscturcure of silica monoliths obtained in the presence of a static (a) of rotating (b) magnetic field.

REFERENCES: M. Furlan and M. Lattuada; **2012**; *Langmuir;* 28:12655-727.

Ion specific effects on layering of nanoconfined salt solutions

S. Liuzzi[1], S. Chodankar[1], R.M. Espinosa Marzal[2], M. Guizar-Sicairos[1], M. Heuberger[2,3] and J. Friso van der Veen[1,2]

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[3] EMPA, 9014 St. Gallen, Switzerland

When a liquid is confined in nanoscopic space, the combination of interfacial effects and size often confer to the system properties much different from those observed in bulk fluids. In particular, understanding the structure of electrolytes nanoscopically confined between two aluminium-phyllosilicates walls could be enlightening in a number of fields, ranging from biology to nuclear waste management, as well as clarify some fundamental issues regarding alkali hydration energies and their influence on the surrounding hydrogen bond network. We have adapted a surface force apparatus (SFA) to be used as confinement device in an X-ray reflectivity (XRR) experiment conducted at cSAXS (XSA12) beamline of the Swiss Light Source at PSI. Two cylinder-shaped muscovite mica membranes were made to approach each other and a flat contact area was formed in which droplets of RbCl, CsCl and $BaCl_2$ solutions at different concentrations were confined.
To achieve such confinement, we had to screen out the double layer repulsion and allow attraction between the mica membranes working at high concentrations with Debye length λ_D<1 nm.
We have performed XRR experiments from the contact area as a function of the momentum transfer q ranging from 0 to 7 Å^{-1}. Model dependent fits to the measured reflectivity $I(q)$ allowed us to determine the minimum gap distance (1.9 nm for RbCl, 1.6 nm for CsCl and 2.4 for $BaCl_2$) and the electron density profile along the confinement direction. The profiles indicate an ordered layering of the liquid within the gap, with the layering being most pronounced for hydrated ions closest to the confining walls. Acomparison between the structures of confined chlorides with different monovalent and divalent cations (Cs^+, Rb^+ and Ba^{2+}) at different concentrations (see figure below) reveals ion specific features which may be linked to ion size, valence and hydration energy.

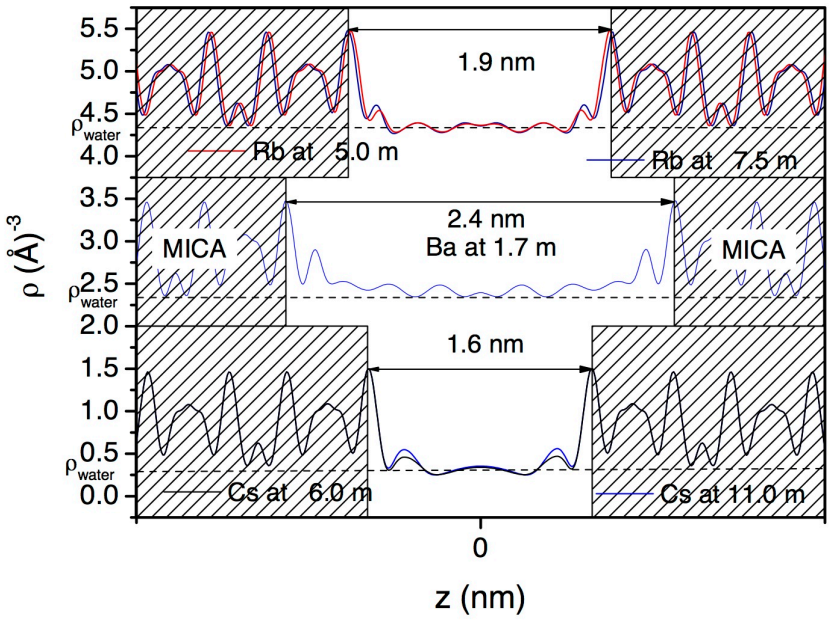

Fig.1: Best-fit electron density profiles for confined RbCl at concentrations of 5.0 m and 7.5 m (up, baseline 4.0), $BaCl_2$ at 11 m (center, baseline 2.0) and CsCl at 6.0 m and 11.0 m (down, baseline 0.0).

Study of the early stage of amyloids fibrils formation in α-synuclein by AFM Single Molecule Statistical Analysis

F. S. Ruggeri[1], *Hilal Lashuel*[2], *Raffaele Mezzenga*[3], *G. Dietler*[1]

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Corresponding author: simone.ruggeri@epfl.ch

Amyloidosis consists in the aggregation of proteins in insoluble fibrous structures with a cross-beta sheet quaternary structure. In particular, amyloidosis of α-Synuclein proteins plays a central role in the Parkinson's disease and the understanding of the mechanisms of fibrils formation can provide the basis for establishing approaches to the disease prevention.
In our work we focused on the analysis of the early stages of the amyloid fibrils formation and the use of the AFM technique becomes essential to unravel the characteristic of our structures at the nanometer single molecule length scale. This has allowed us to follow in detail the initial aggregation path and to resolve the moment in which monomers are assembling to form the first pre-fibrillar aggregates. If we incubate our protein at 37 C° in a test tube, at 0 hours we see just monomers and oligomers on our surface (Fig. A). With increasing incubation time, figure (B) and (C), elongated structures start to form, we will call them Protofilaments and they belong to two families of height: 0.3 nm and 0.7 nm. Considering the monomers dimensions we can affirm that the first family is composed by a single monomeric layer and we will call it **Single Strand** protofilament, while the second one, formed by two single strands joining together will be called **Double Strand Protofilaments**. Lower height population has not periodicity while the taller one has a periodicity of 8 nm. (Fig. D)

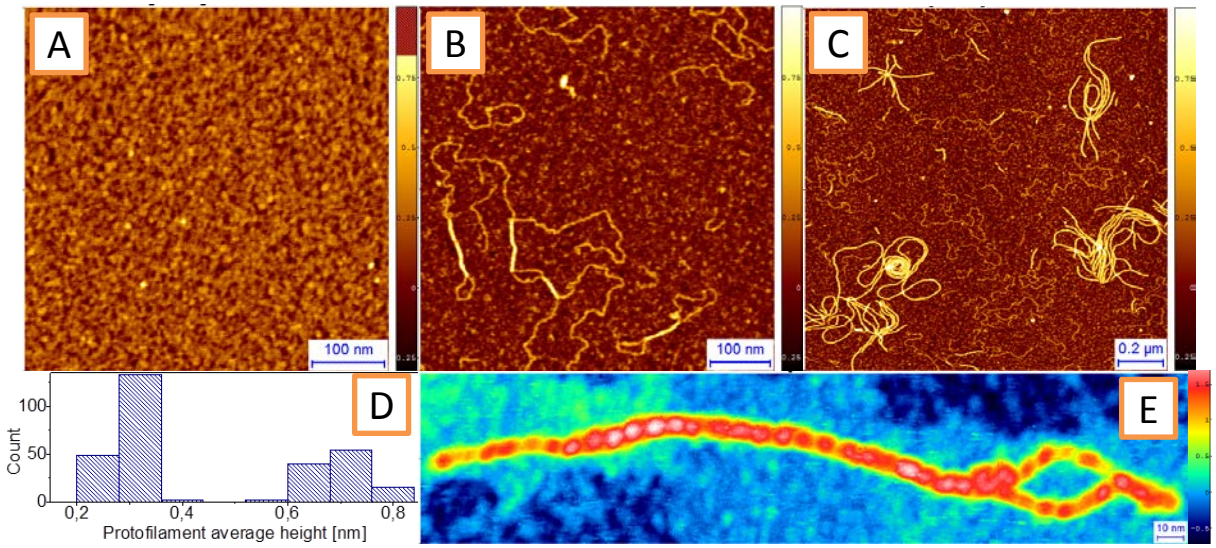

Figure 1 Protein's aggregation path and morphology, AFM tapping mode images in air. (A) 0 hour: monomers and oligomers covering the surface. (B) Single strand protofilaments start to form and to join (C) Single strand protofilaments stabilize; double strand ones elongate. (D) Distribution of the average height of the protofilaments. (E) Detail of two double strand protofilaments joining, they show a periodicity of 8 nm.

The shown aggregation pathway it is in fully agreement with the Hierarchical Assembling Model in which it is suppose the existence of protofilaments which join together to form the mature fibrils. Moreover, a theoretical approach of statistical polymer physics allowed us to investigate the mechanical properties of the protofilaments; the lower and higher height populations show respectively a persistence length of 20 nm and 200 nm. Next step of our study will be continuing to follow the aggregation path to unravel it, to evaluate the internal structure of our molecules and measuring theirs Young's modulus.

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Non-equilibrium nature of 2D isotropic and nematic coexistence in amyloid fibrils at liquid interfaces

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INTRODUCTION: Two-dimensional (2D) alignment of shape-anisotropic colloids is ubiquitous in nature, ranging from interfacial virus assembly to amyloid plaque formation. The principles governing 2D self-assembly have therefore long been studied, both theoretically and experimentally, leading, however, to diverging fundamental interpretations on the nature of the 2D isotropic-nematic phase transition.

METHODS: We employ passive probe particle tracking[1], Atomic Force Microscopy (AFM) and Freeze-fracture Shadow-Casting Scanning Electron Microscopy (FreSCa cryo-SEM)[2] to study the adsorption-governed 2D LC ordering of highly anisotropic semiflexible *β*-lactoglobulin amyloid fibrils at air-water and oil-water interfaces. We evaluate this alignment with a length scale-dependent 2D order parameter $S_{2D}(d)$ and determine the amount of nematic coverage at the interface.

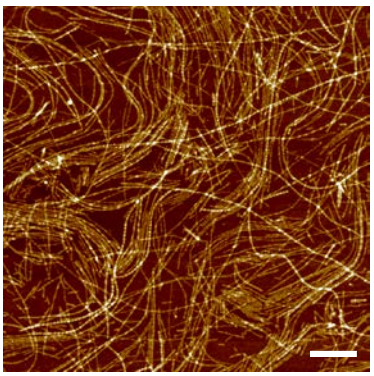

Fig. 1: AFM image of fibrils adsorbed at the air-water interface (scale bar = 500 nm).

RESULTS: All three techniques concurrently show that nematic fibril domains form upon increase in interfacial density ρ (Fig. 1). Analysis the fibrils' end-to-end distance as a function of contour length reveals that their bending length changes as a function of LC ordering and crowding.

The decay of the order parameter on each image $S_{2D}^{image}(d)$ is a sum of the weighted components S_{2D}^{align} and S_{2D}^{rand}, accounting for aligned and random fibril domains, respectively.

The fraction of nematic domains *a* is shown to increase as a function of adsorption time. Intriguingly, higher alignment is observed for interfaces generated by adsorption from more dilute solutions (Fig. 2).

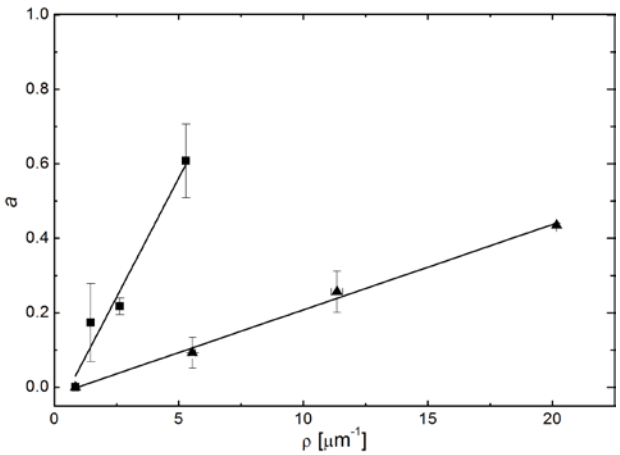

Fig. 2: The fraction of aligned fibrils depends on the initial bulk concentration. Weighting factor a as a function of ρ for c_{init} = 0.001% w/w (■) and c_{init} = 0.005% w/w (▲).

DISCUSSION: Fibrils align in 2D solely due to passive adsorption onto a liquid interface. Their end-to-end distance is shown to depend on the local density at the interface: Alignment causes fibrils to straighten, but as soon as the interfacial fibril coverage becomes so high that whole domains are forced to undergo in-plane bending, this value decreases again. This evolution in a crowded environment suggests that, both, excluded volume and pairwise interactions contribute to the change in fibril conformation.

The nematic surface fraction increases with interfacial fibril density, but depends, for a fixed interfacial density, on the initial bulk concentration. In view of the irreversibility of fibril adsorption to the liquid interface, we ascribe the observed 2D isotropic-nematic coexistence to non-equilibrium phenomena.

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Collective processes in the adsorption of nanoparticles at liquid-liquid interfaces

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The properties of composite materials arise from the interplay of the different components via the interfaces between them as well as from the bulk properties of the constituents. Self-assembly of nanoparticles at liquid-liquid interfaces stirs great interest as a novel route to tune material properties at the nano-scale, although there is still limited understanding of how to control the adsorption process and its effect on the interface development.

We present a numerical approach to investigate the adsorption of polydisperse soft shell particles onto a liquid-liquid interface. The nanoparticles are modeled as soft-spheres and for the adsorption-desorption process we use a Grand Canonical Monte Carlo scheme. The particle dynamics at the interface is investigated via Molecular Dynamics.

By analyzing the evolution of structure and dynamics upon adsorption of polydisperse and monodisperse particles, we gain significant insight into the role of slow dynamics, development of local or long-range order and jamming at the interface. Some of these findings can be used to rationalize recent experimental observations (1,2).

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Abstractd for the poster

Magnetic silica platelets produced in rotating magnetic field

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There is a growing interest in producing composite materials made of inorganic reinforcing blocks entrapped in organic polymer matrices. Such kind of composites can be produced either by top down or bottom up approaches. Between the two, the bottom up approach is the most promising one, especially in combination with self-assembly. Conscious of the intrinsic limitations encountered with isotropic particles, many scientists are working on the preparation of anisotropic building blocks such as rods, stars, platelets etc., in order to increase the possible structures that can be formed by self-assembly.

In this work we present a new method to prepare magnetic silica platelets by assembly of polymer magnetite nanoparticles under the influence of a rotating magnetic field. Superparamagnetic nanoparticles where first prepared via miniemulsion polymerization. Magnetite nanocrystals, previously hydrophobized with ricinoleic acid, were first dispersed in the monomer mixture and then miniemulsified with a water surfactant mixture. Pluronics was chosen as surfactant in order to improve the dispersibility of the particles in the reaction mixtures during the second step. In the second step the particles are dispersed in a mixture of acidic water pre-hydrolyzed and tetramethoxy silane (TMOS), a silica precursor. The obtained mixture was then poured in a mold and placed between the poles of an electromagnet. The sample was then rotated inside the uniform magnetic field in order to mimic a rotating magnetic field.

Under the influence of a rotating magnetic field the superparamagnetic particles assemble themselves into monoliths made of sheet-like structures held together by few linking points as can be seen in Fig. 1. By applying strong sonication these few links can be easily broken and platelets of a size between 20 and 50 µm can be obtained.

The formation of these peculiar structures is due to the strong affinity of silica towards magnetite, so that the silicon precursor condenses on the nanoparticles leading to a partially or even complete coverage of particles. The particles are then connected by the polymerization of the silica leading to the formation of the platelet structures. As shown in a previous publication [1], the addition of a small amount of polyethylene glycol (PEG) results in a different final morphology of the platelet due to the spinodal decomposition induced in the system.

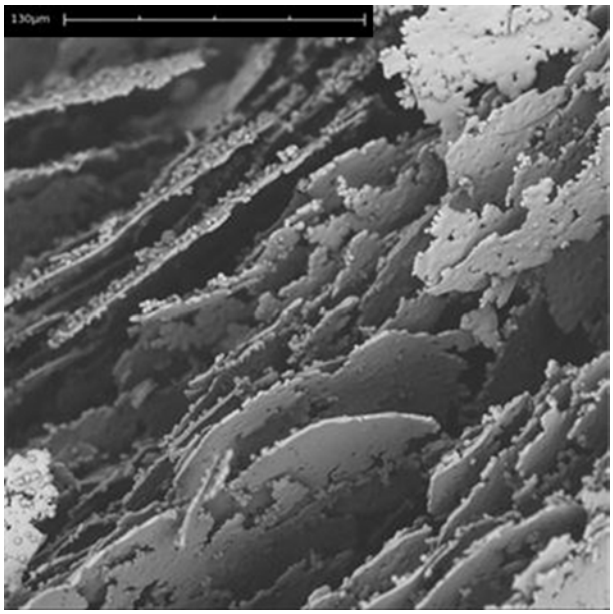

Fig. 1: SEM pictures of a monolith produced in rotating magnetic field.

The rotational speed of the sample inside the magnetic field is of paramount importance for the formation of the platelets. Very slow speed such as few rpm leads to the formation of curved tubular structures. Speed between 10 to 100 nm leads to the formation of oval-shaped structures entrapped in a random silica structure. Instead if the speed is more than 200 rpm platelets are produced. In the system with PEG the thickness of the platelets can also be tuned. By varying the ratio between PEG and magnetic nanoparticles the thickness of the platelets can be changed between several hundreds of nanometers and few micrometers.

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Abstract

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A. Fernandez-Nieves[3]

Effect of polydispersity on the phase behavior of soft microgel suspensions

Microgel suspensions with a majority of small particles and a small fraction of big particles with about double size can form crystals without defects caused by the large particles. Due to the softness of microgel particles, the big particles can shrink to fit into the lattice formed by the small particles (A. St. John Iyer and L.A.Lyon, Angew. Chem. Int. Ed. , 48, 4562-4566, 2009). For hard spheres, the size-polydispersity is a much more limiting factor for crystallization. No hard sphere crystals form at polydispersities higher than 12%. We systematically study the role of polydispersity in suspensions of fully swollen poly(N-isopropylacrylamide) (pNIPAM) microgel particles. Small-angle neutron scattering (SANS) and dynamic light scattering are used to measure polydispersity, particle size and the internal structure of the particles in suspensions with polydispersities in the range from 10% up to 20%. We observe crystallization in samples with polydispersity as high as 17%. Furthermore, the effect of polydispersity on the crystal lattice is obtained from SANS and small-angle X-ray studies.

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Synthesis of Dumbbell Anisotropic Nanoparticles by Seeded Emulsion Polymerization

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Over the last years, research focusing on anisotropic materials gained much interest in the scientific community, due to their intriguing properties and promising applications.

In opposition to spherical particles which only have limited features, non-spherical objects display much more interesting behaviour due to their geometrical features. In spite of the intrinsic interest in non-spherical nanoparticles, systematic strategies to prepare them are still lacking.

The work presented here describes a multi-step emulsion-based process that can be used to produce large quantities of dumbbell like nanoparticles. The strategy used to produce these nanoparticles is based on a double-seeded emulsion polymerizations starting with narrowly-distributed polystyrene (PS) seeds [1].

The first seeded-emulsion polymerization is carried out in order to form a shell of a random copolymer of styrene (St) and 3-trimethyloxysilyl propyl acrylate (MPS). The shell, containing silane groups on the surface, has two roles: increasing the hydrophilicity of the nanoparticles surface and providing reactive sites for further chemical functionalization of the nanoparticles.

The second seeded-polymerization step involves the swelling of the core-shell nanoparticles with additional monomer. As the polymerization proceeds, the hydrophilic shell will prevent the newly formed polystyrene to simply swell the particles, but will force it to bulge apart from the original seed. The final particles are composed of a dumbbell containing a first hemispheres bearing silane group on the surface, while the second bulge is pure polystyrene. The silane-functionalized hemispheres can be further functionalized by reaction on the silane groups. A silica shell could be deposited on the surface of one hemisphere by the hydrolysis and condensation of silica precursor, giving birth to an organic-inorganic shape-anisotropic nanoparticle.

The final shape and size of the nanoparticles depends on many parameters. The size of the first hemisphere can be tuned using PS seeds of different diameter. The relative size of the two bulges can be adjusted by playing with the swelling ratio in the last step. The thickness of a silica shell could also be changed by taking different amounts of silica precursor.

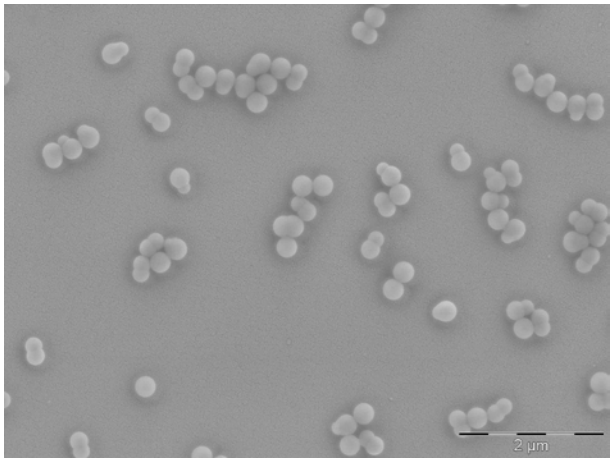

Figure 1: Scanning Electron Microscopy image of Dumbbell Anisotropic Polystyrene Nanoparticle

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Structure and kinetics of α-lactalbumin particulates

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Protein molecules are prone to self-assembleing, when heated, into structures that depend on their net charge. While proteins self-assemble into fibrils in conditions of high net charge, they form large spherical aggregates/ particulates around their isoelectric point.[1, 2] We have investigated the aggregation behavior of α-lactalbumin, a calcium-binding protein, in conditions of very low net charge. Using a combination of modulated 3D cross-correlation static and dynamic light scattering and small angle light scattering, we show that α-lactalbumin molecules self-assemble into spherical aggregates at low concentrations (0.3-1mg/ml) and temperatures (37-55°C). We follow the kinetics of formation of the particulates and measure their internal dynamics and structures.

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Studying Complex Nanoparticle Self-Assembly at Liquid Interfaces Using Pendant Drop Tensiometry and Microrheology

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

It has recently been demonstrated in our group that superparamagnetic iron oxide nanoparticles (NPs) stabilized by low molecular weight poly(ethylene glycol) (PEG) shells [1,2], can indeed be self-assembled into saturated monolayers at the water/*n*-decane interface [3,4].

Understanding the basics of SALI is a keystone in turning these NP assemblies into composite membranes suitable for applications. In particular, measuring the viscoelastic properties of the interfacial assemblies *in situ* and on the micro-scale is of paramount importance.

METHODS: Nanoparticles with a 7.3 nm diameter core of Fe_3O_4 with a linear PEG shell, M_w = 2737 g/mol [2] were used for these investigations. Polystyrene particles with a diameter of 2.8µm and labelled with FITC were used as tracers in microrheological experiments.

NPs were suspended at different concentrations in milliQ water, then an interface with *n*-decane was formed.

Characterisation using pendant drop tensiometry (PDT) has been completed at different NP concentrations in order to investigate the kinetics of particle adsorption to the interface.

Figure 1 shows the setup used for microrheology, during formation of the *n*-decane-water interface some tracers are trapped at the interface. The nanoparticles adsorb to the interface with time. Time lapse images show the tracer motion. Analysis of the mean square displacement gives the diffusion coefficient:

$$\left\langle x^2 + y^2 \right\rangle = 4Dt$$

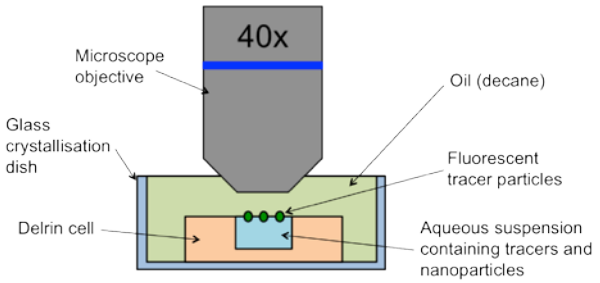

Fig. 1: Basic setup for microrheology using fluorescence microscopy.

RESULTS: PDT shows that interfacial tension, γ, decreases with NP adsorption. Different concentrations change the speed of adsorption, but they achieve the same final interfacial tension, indicating irreversible adsorption of nanoparticles, forming a saturated monolayer.

In microrheology experiments, particle tracks over 30 minutes show mostly Brownian behaviour (random walk). The mean square displacements show diffusive behaviour, with and without nanoparticles. Average values for the diffusion coefficient show a significant difference between measurements with and without NPs.

DISCUSSION & CONCLUSIONS: PDT shows a concentration dependence of speed of nanoparticle adsorption to form a dense monolayer at the interface.

A setup has been developed to characterise the adsorption of nanoparticles to an oil-water interface. The setup has been used to demonstrate that the diffusion coefficient at interface changes upon adsorption of nanoparticles.

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Cononsolvency: the hallmark of a transition between solvation mechanisms

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INTRODUCTION: Poly-N-isopropyl acrylamide (PNiPAM) exhibit the rather rare phenomenon of cononsolvency [1]. At T=20°C, PNiPAM is perfectly soluble in both pure water and pure alcohol; however, the polymer is insoluble in certain mixtures of the two solvents. This impressive phenomenon is illustrated in Fig.1a, where we show a series of images of PNiPAM in water-methanol mixtures with varying methanol molar fraction X_{MeOH}: within an intermediate range of X_{MeOH} (~0.15−0.4) the solutions are turbid, clearly indicating that PNiPAM is insoluble at these conditions, while out of this range the solutions are clear, indicating that PNiPAM is soluble.

Experiments aimed at probing the PNiPAM dimensions in these water-alcohol mixtures reveal the presence of a reentrant coil-to-globule-to-coil transition [2] (Fig.1b), with boundaries that are clearly correlated to the range of methanol concentrations showing a solubility gap.

The reason why a mixture of two *good* solvents for the polymer could result in a *non*-solvent, even though the solvents by themselves are miscible in all proportions, is still a matter of debate.

METHODS: We explore the origin of the cononsolvency phenomenon of PNiPAM solutions in respectively water/methanol and water/ethanol mixtures by systematically studying the temperature-dependent phase behaviour of PNiPAM as a function of solvent composition. For this purpose we place our samples in a home-made temperature cell allowing a temperature control precision of ± 0.1°C over a temperature range of -20°C to 60°C. The onset to insolubility at the critical solution temperature T_c is determined by visually assessing the onset to turbidity. In addition, we characterize the temperature dependent dimensions of PNiPAM-microgels in static light scattering, where we determine the radius of gyration, R_g, from the angular dependence of the scattered intensity, $I(q)$, over a range of scattering wave vectors from q = 8 μm^{-1} to q = 30 μm^{-1}.

RESULTS: Our findings indicate that the phenomenon of cononsolvency can be understood as the result of a transition between solvation mechanisms. At high water content the solvation of PNiPAM is primarily determined by the enthalpic gain of water, solvating PNiPAM via hydrophobic hydration. At high alcohol content, instead, the solvation of PNiPAM is driven by the gain in mixing entropy that generally determines the thermodynamics of solutions. Cononsolvency is observed in the transitional range between these two solvation mechanisms, where neither the gain in water enthalpy nor the gain in mixing entropy upon solvation of PNiPAM is prevailing.

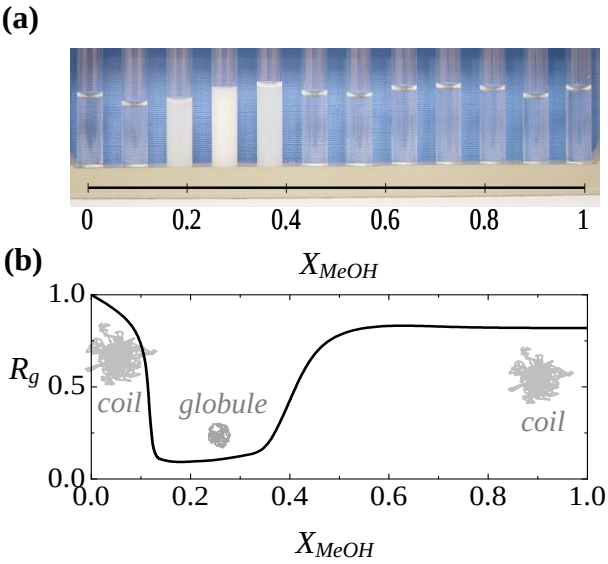

Fig. 1: (a) Phase behaviour of PNiPAM in water / methanol mixtures as a function of the methanol molar fraction X_{MeOH} at a fixed temperature of T=20°C. Despite being soluble in pure water (extreme left) and pure methanol (extreme right) the polymer is insoluble within an intermediate range of alcohol concentrations. (b) Schematic of the dependence of the radius of gyration on methanol content obtained at fixed temperature. The schematic is drawn from the data obtained by Wu et al [2]: a clear correlation is visible between solubility and conformation change of the PNiPAM.

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Melting Temperature and Crystal Growth Rate in Liquid Mixtures

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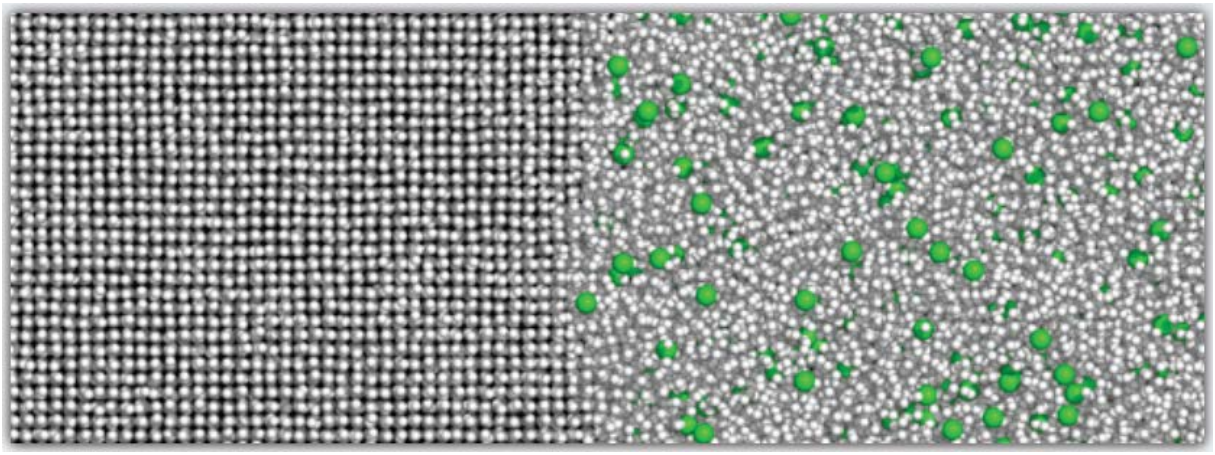
Crystallization of liquids is of uttermost interest for many disciplines, including materials, atmospheric and food science. The introduction of additives in solution allows the control of the key thermodynamics and kinetics parameters of crystallization, namely the transition temperature and the growth rates. Here we investigate the basic principles of crystallization of solutions by computing the melting temperature and simulating crystal growth of Lennard-Jones binary mixtures, by equilibrium and non-equilibrium molecular dynamics (EMD - NEMD) simulations. Both melting temperatures and growth rates are computed exploiting the two-phase method at equilibrium and non-equilibrium conditions, respectively. The effect of hydrophobic and hydrophilic solutes at low concentrations (< 3%) is analyzed, scanning systematically size and concentration. Our MD simulations allow us to connect macroscopic thermodynamic and kinetic observables, such as phase coexistence temperature and crystal growth rate, to the microscopic structure of the solutions and to microscopic processes occurring during crystal growth.



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Micro-Rheological Characterization of Emulsions

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[1] *Fachhochschule Nordwestschweiz, Institute of Pharma Technology, Basel, Switzerland.*

[2] *LS Instruments, Fribourg, Switzerland.*

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 [3,4]. 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.

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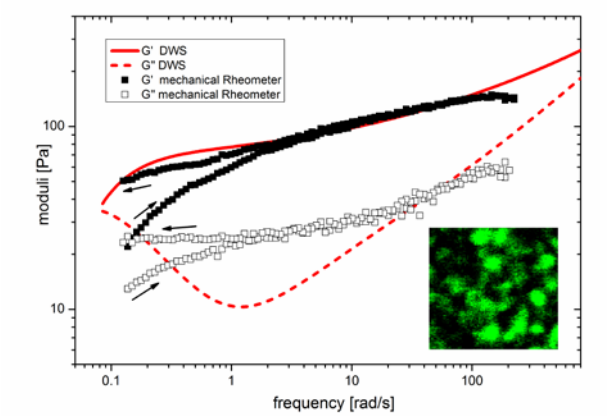

Fig. 1: Comparison of elastic modulus G' and viscous modulus G" obtained from DWS and mechanical rheometer. The arrows show the order in which the mechanical data has been measured. The inset shows a 3x3µm large confocal image from the emulsion.

DISCUSSION & CONCLUSIONS:

DWS based microrheology seems ideally suited for the characterization of emulsions because of their high turbidity and high 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.

NANOSCALE NUMERICAL STUDY OF C-S-H PRECIPITATION AND GELATION

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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.

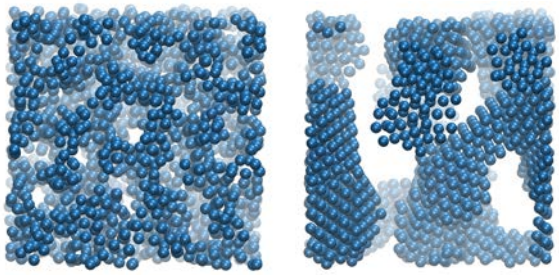

Fig. 1: Microstructures of the mesoscale gel model for C-S-H, at density ρ=0.25 and temperature T=0.3, for two different effective interactions in equilibrium.

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Thermoresponsive-biopolymer blends as bio-inks for cartilage engineering

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INTRODUCTION: Extrusion bioprinters are nowadays commercially available and technologically advanced. Despite this, there is still a lack of suitable materials, so called bio-inks. The ideal bio-ink for extrusion printing should be liquid at the beginning to mix it freely with other polymers, peptides or cells and have a flow behavior that is compatible with the extrusion process. For printing fidelity, cessation of flow upon deposition is necessary. The final construct should also have similar mechanical properties as the surrounding tissue. Our study investigates the properties of polymer blends suitable for bio-inks in extrusion bioprinting. Material blends of thermoresponsive and photopolymerizing polymers provide improved properties for printing compared to the individual components. In fact, these blends have the capability of tandem gelation i.e. two gelling steps where in the first step the right viscosity for printing is achieved whereas in the second step a mechanically robust gel is produced that can be used for cartilage repair.

METHODS: A methacrylated derivative of Pluronic F127 (PF127) or hyaluronic acid grafted Poly(*N*-isopropylacrylamide) (HA-PNIPAM) (AO Research Institute Davos, Switzerland) were used as the thermoresponsive elements of the bio-ink. Methacrylated Pluronic F127 and HA-PNIPAM were blended with methacrylated hyaluronic acid and methacrylated chondroitin sulfate to improve mechanical properties of the final gel and to include biological cues. The bio-inks were analyzed with an Anton Paar MCR301 rheometer utilizing a cone-plate geometry. Flow curves were recorded to test the printability of the gels while temperature ramps and UV crosslinking under oscillation were performed to investigate the gelling kinetics of the two gelation steps. Initial chondrocyte and mesenchymal stem cell viability was assessed with a live/dead assay one day after the encapsulation in the PF127-biopolymer hydrogel blends.

RESULTS: Chondrocytes as well as mesenchymal stem cells have shown good viability (>70%) after one day of culture within the Pluronics hydrogel (25% w/v) blended with 5% w/v chondroitin sulfate. The cell viability, however, is not the only criterion considered for the bioprinting process. The rheological measurements of non-methacrylated Pluronic blended with chondroitin sulfate reveal that the gelation temperature of the Pluronic is increased upon the addition of 5% chondroitin sulfate (see Fig. 1). In detail, the gelation temperature is raised from initially 16.8°Cto 38.6°C and is therefore shifted to temperatures above room temperature.

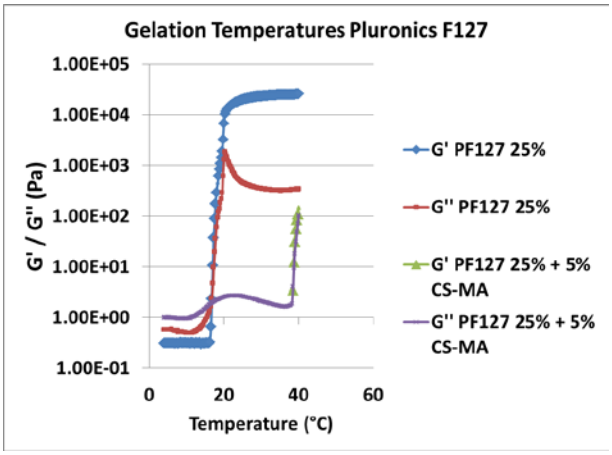

Fig. 1: Temperature ramp of Pluronic F127 with or without the addition of biopolymer chondroitin sulfate. The addition of the biopolymer shifts the gelation temperature of Pluronic to higher temperatures (green and purple line).

DISCUSSION & CONCLUSIONS The addition of biopolymers has been shown to influence the gelation temperature of Pluronic and biocompatibility of the material. In particular, the addition of 5% chondroitin sulfate caused an increase in cell viability to <70%. The gelation temperature, however, was increased above room temperature, thus necessitating the use of a heated stage for accurate extrusion printing of this bio-ink. Given the fact that other biopolymers with different charge and molecular weight than chondroitin sulfate can be mixed with Pluronic or HA-PNIPAM, we hypothesize that other combinations might produce a smaller shift in the gelation temperature, thus proving to be even more cell-friendly and suitable for bio-printing.

ACKNOWLEDGEMENTS: We thank Prof. Peter Fischer for the help with the rheological measurements.

Tracking up-conversion nano-phosphors and superparamagnetic iron oxide nanoparticles in aquatic plants: ESR and confocal microscopy assays

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INTRODUCTION: Nanotechnologies represent a rapidly growing field which exploits nano-engineered materials having novel characteristics, occurring only at the nanoscale. The properties of nanomaterials that make them useful in a wide range of industrial applications have also led to concerns regarding their potential impact on human and environmental health. The aquatic environment is particularly at risk of exposure to man-made nanoparticles, as it acts as a sink for most environmental contaminants. Up-conversion nano-phosphors (UCNPs) and superparamagnetic iron oxide nanoparticles (SPIONs) have been widely used in bioscience and bioimaging, but their uptake and internalization by plants have been studied to a much lesser extent [1-2]. The key property of UCNPs is their ability to up-convert near-infrared (NIR) light into visible light, thus offering numerous advantages of nonlinear excitation for biomedical imaging, including lack of background fluorescence, increased tissue penetration for depth-resolved imaging, and reduced risk for photo-damage. The major advantage of SPIONS is their high responsivity to alternating and constant magnetic fields, which makes them extremely useful in various biomedical applications, including contrast agents in magnetic resonance imaging (MRI), drug delivery, tissue repair, hyperthermia, and *in vivo* cell tracking.

METHODS: Herein, we took advantage of the characteristic properties of UCNPs and SPIONs to track their uptake and internalization by selected higher aquatic plants. In particular, we applied electron spin resonance (ESR) to follow penetration and translocation of citric acid functionalized 10-nm γ-Fe_2O_3 SPIONs in *Elodea Canadensis* and *Vallisneria Spiralis*. Moreover, we also implemented confocal microscopy with the use of NIR light for excitation to follow the uptake and internalization of non-functionalized 500-nm $NaYF_4$:Yb,Er UCNPs in *Elodea Canadensis*.

RESULTS: The ESR measurements performed on *Elodea Canadensis* and *Vallisneria Spiralis* exposed to waterborne SPIONs demonstrated that these particles could penetrate into plants both *via* the roots as well directly into the plants leaves. Moreover, confocal microscopy showed that non-functionalized $NaYF_4$:Yb,Er UCNPs were able to enter the roots of *Elodea Canadensis*, thus pointing to a long distance particle translocation - despite the relatively large size of the particles used in this study (~500 nm).

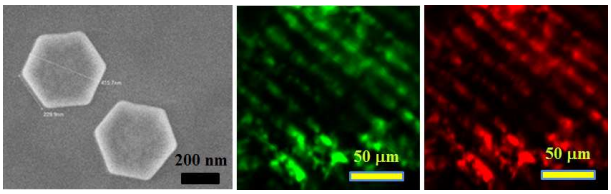

Fig. 1: Highly-luminescent $NaYF_4$:Yb,Er UCNPs used in confocal microscopy experiments with aquatic plants (left); green and red up-converted luminescence of the internalized UCNPs in the roots of Elodea Canadensis (right).

DISCUSSION & CONCLUSIONS: Our findings indicate that ESR and confocal microscopy represent two prospective powerful techniques to quantify and visualize the uptake of nanoparticles into aquatic plants.

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WORM-LIKE micelles as a template for polymerization

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The use of particles with anisotropic shape is of significant interest since it allows fabrication of structures with special symmetries and degree of packing and/or anisotropic properties[1]. Rod-like polymer particles could have interesting properties and could find many practical applications; however, few methods for the production of such particles are available. They are usually produced by templating inside the pores of membranes or zeolites, with resulting size and volume production limited by the template capacity. In the current work we introduced and investigate a simple method for synthesis of a new class of polymeric nanorods based on a semi-batch emulsion polymerization using wormlike micelles as template.

Amphiphiles can self-assemble in solutions giving rise to various structures or aggregates such as spheroidal, worm-like micelles, vesicles and bilayers. Surfactant molecules generally form spherical aggregates in aqueous solutions above a critical concentration. However, under appropriate conditions of concentration, salinity, temperature, size of their counterions these small spherical micelles can undergo uniaxial growth to form wormlike micelles, which are elongated and semiflexible aggregates[2]. In the case of Cetyl trimethyl ammonium Tosylate (CTAT) the morphological transition from spherical to cylindrical micelles can be attributed to an increased binding of the tosylate counter-ions to the quarternary ammonium headgroups. This leads to a decrease of the headgroup repulsion and hence an increase of the packing parameter[3].
In the current work, the solubilization and polymerization of MMA, STY and DVB in CTAT wormlike solution was investigated and characterized by TEM, SEM and SAXS technique.

Semi-batch emulsion polymerization has been successfully performed with a continuous feeding of monomer through a syringe-pump and both spherical and elongated particles have been formed, in a ratio depending upon several factors, especially polymer concentration and monomer feeding rate.

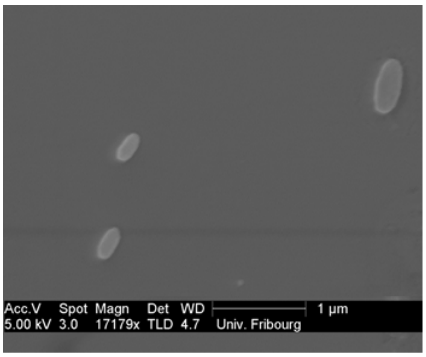

Figure 1 SEM image of pSTY elongated nanoparticles.

Therefore, the presented approach represents a possible method for the production of anisotropic particles, with the purpose of studying their assembly for the preparation of nano- and microstructured materials.

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Title

Enhanced tunneling conductivity induced by gelation of attractive colloids

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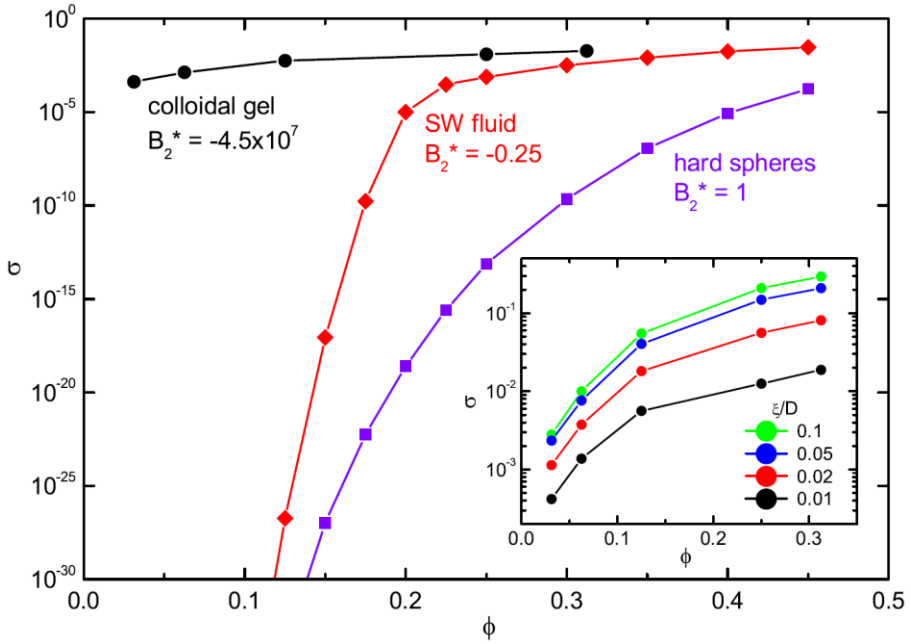
Abstract

We show that the formation of a gel by conducting colloidal particles leads to a dramatic enhancement in bulk conductivity, due to inter-particle electron tunneling, combining predictions from molecular dynamics simulations with structural measurements in an experimental colloid system. Our results suggest that gelation is a general route to huge enhancement of conductivity in systems of colloidal particles, potentially enabling the development of materials with novel properties.



Recognition of Imipenem and Meropenem by the RND-Transporter MexB Studied by Computer Simulations

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Active extrusion of drugs through efflux pumps constitutes one of the main mechanisms of multidrug resistance in cells. In recent years, large efforts have been devoted to the biochemical and structural characterization of RND efflux pumps in Gram-negative bacteria, in particular the AcrB/A-TolC system of E.Coli. Specific attention has been addressed to the active part of the efflux system, constituted by the AcrB unit1-5. Crucial questions concerning its functioning are still open. The understanding of the structure-dynamics-function relationship of MexB, the analogous transporter in P. Aeruginosa, encounters even more difficulties, because of the lack of structural data of the transporter in complex with substrates. To shade some light on the activity of MexB, we performed computational studies on MexB interacting with two compounds, meropenem and imipenem, the first known to be a good substrate, and the second a modest one. Several techniques were used in the present work, ranging from flexible docking6 to MM-PBSA and standard molecular dynamics (MD) simulations. Starting from the published crystal structure7 we identified the most probable poses of the two compounds in the original experimental structure. The available information on the binding pocket of AcrB has guided the choice of the putative affinity site of meropenem and imipenem in MexB.

A coarse-grained model for numerical simulations of proteins

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We present a new generation of coarse-grained (CG) potentials that account for a simplified electrostatic description of soluble proteins. The treatment of permanent electrostatic dipoles of the backbone and polar side-chains allows to simulate proteins as long as 200 amino acids, preserving an excellent structural and dynamic agreement with respective reference structures and all-atom molecular dynamics simulations. Moreover, multi-protein complexes can be well described maintaining their molecular interfaces thanks to the ability of this scheme to better describe the actual electrostatics at a CG level of resolution. An efficient and robust heuristic algorithm based on particle swarm optimization is used for the derivation of CG parameters via a force-matching procedure. The ability of this protocol to deal with high dimensional search spaces suggests that the extension of this optimization procedure to larger datasets may lead to the generation of a fully transferable CG force field. At the present stage, these electrostatic-consistent CG potentials are easily and efficiently parameterized, show a good degree of transferability and can be used to simulate soluble proteins or, more interestingly, large macromolecular assemblies for which long all-atom simulations may not be easily affordable.

Amyloid fibrils: insights from all-atom simulation

Martina Audagnotto, Enrico Spiga , Matteo Dal Peraro
EPFL LBM

The pathogenic aggregation of the amyloid is considered a hallmark of the progression of different disease (Alzheimer's disease, Parkinson's disease, Huntington's, familial British and Danish Dementia's) in which the protein present an abnormal folding of peptides.
Starting from the X-ray classification made by Eisenberg for the possible core structure of the amyloids, we studied all the 8 classes proposed employing All-Atom molecular dynamic simulation. We discriminate against structural parameters and energetics, finding that the increase of the number of strands (the single beta sheet which compose the all structure) corresponds to an enhanced stability.