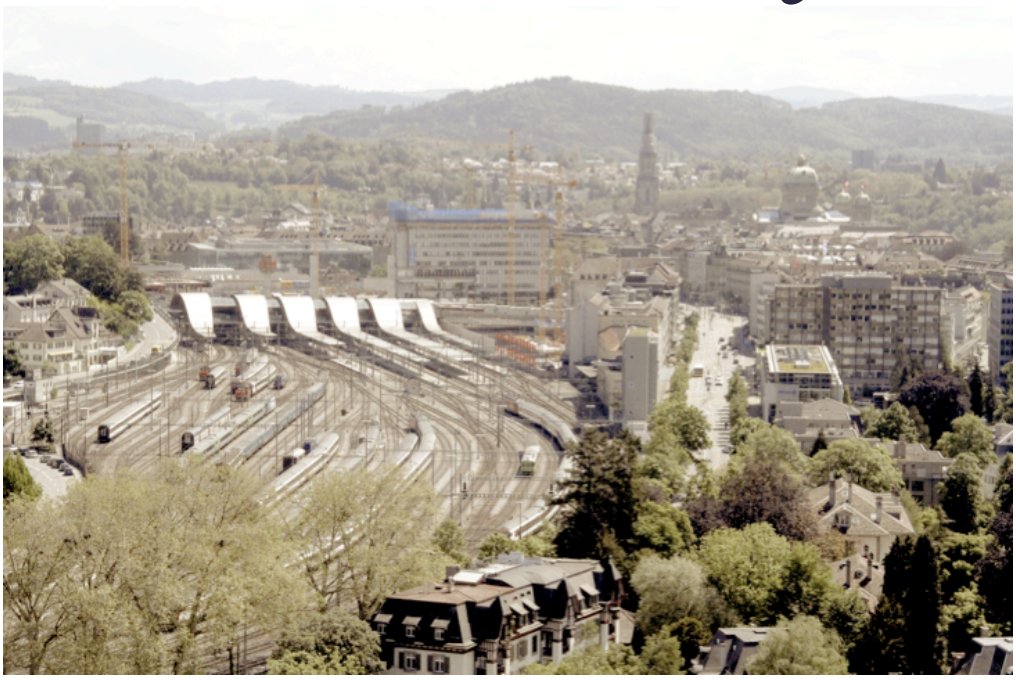
Bern, 14th October 2013

Swiss Soft Days 12



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BERN

Schedule

9:50-10.15 Registration and Coffee

			10.15-11.00
Welcome	J.Czerwinska	Uni Bern	10.15-10.20
Application of nanofibres for biomedical diagnostics and therapy.	T. Kowalewski	IPPT Warsaw Poland	10.20-11.00
Rheology of complex systems	Chair	V. Trappe Uni Fribourg	11.00-12.20
Microscopic mechanism for the shear-thickening of non-Brownian suspensions	N. Fernandez	ETHZ	11.00-11.20
Phospholipid bicelles to generate magnetically switchable material	P. Fischer	ETHZ	11.20-11-40
Liquid-crystalline elastomer - nanoparticle hybrids with reversible switch of magnetic memory	J. M. Haberl	ETHZ	11.40-12.00
Bacterial hydrophobicity and biofilm formation at water-oil interfaces	P. A. Ruehs	ETHZ	12.00-12-20

12.20-14.00 Lunch and Poster Session

Soft matter in medicine	Chair	D. Uehlinger Uni Bern Hospital	14.00-15.00
Arthrosis - when cartilage fails	S. Reichenbach	Uni Bern Hospital	14.00-14.20
The use of colloid osmotic substances as blood plasma expanders	S. Jakob	Uni Bern Hospital	14.20-14.40
Silicon implants - advantages and medical risks	M. Constantinescu	Uni Bern Hospital	14.40-15.00
A label-free serum test measuring overall calcification inhibition	A. Pasch	Uni Bern Hospital	15.00-15.20
Nanocarriers	Chair	C. Palivan Uni Basel	15.20-16.00
A study of the ligand exchange on gold nanorods leads to a hydrophobic drug nanocarrier	C. Kinnear	Uni Fribourg	15.20-15-40
Polymer-aptamer hybrid emulsion templating yields bio-responsive nanocapsules	D. Kedracki	Uni Geneva	15.40-16.00

16.00 -16.40 Poster Session and Coffee

Suspenssion structures and detection methods	Chair	E. Del Gado ETHZ	16.40-18.00
A mechanical sensor to study movement at the nanoscale	G. Longo	EPFL	16.40-17.00
Transient formation of bcc crystal in suspensions of pNIPAM-based microgels	U. Gasser	PSI	17.00-17.20
Laccase encapsulating polymersomes for catalysed biotransformation	M. Spulber	Uni Basel	17.20-17.40
Effect of size polydispersity on the phase behaviour of soft microgel suspensions	A. Scotti	PSI	17.40-18.00
Final remarks	P. Fischer	ETHZ	18.00-18.10

18.30 – Get together at Turnhalle

Poster Presentations

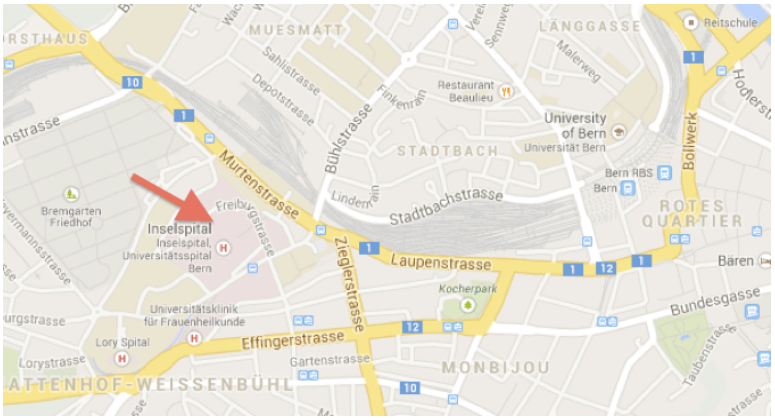
Crowding and ordering in the adsorption of nanoparticles at liquid-liquid interfaces	K. Schwenke	ETHZ
Water flow in highly confined graphene oxide channels	S. Wuest	Uni Bern
Switchable transport across modified membrane channel proteins	C. Edlinger	Uni Basel
Liquid-crystalline elastomer micropillar array for haptic actuation	A. Sanchez-Ferrer	ETHZ
Pumping of blood in capillary networks	A. Renggli	Uni Bern
Interfacial activity of colloidally stable Janus-like silver nanoparticles by pendant drop tensiometry and direct deposition.	M. A. Fernandez Rodriguez	Uni Granada, Spain
Thermo-responsive peptide-based triblock copolymer hydrogels	A. Sanchez-Ferrer	ETHZ
Modern microscopy techniques for biological studies Lifetime (FLIM) and super resolution (STORM) imaging of Drosophila	G. Scalia	Uni Fribourg
Artificial compaction and decompaction of DNA	N. Strelnikova	Uni Basel
Networks of patchy colloids on substrates	N. A. M. Araujo	ETHZ
Polymer membranes functionalized with aquaporins for applications in engineering and biology	F. Itel	Uni Basel

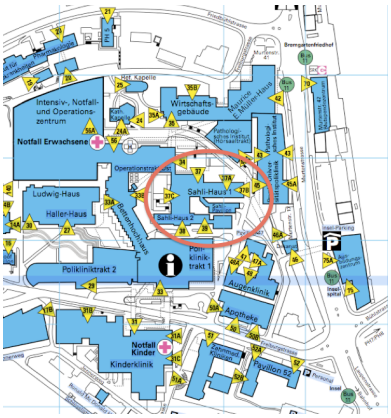
Poster Presentations (cont.)

Simulations of breakage and restructuring of colloidal aggregates in the presence of repulsive interactions	Z. Ren	Uni Fribourg
Reorganizations in the ultrastructure of the thylakoid membranes of Chlamydomonas reinhardtii cells upon state transitions	G. Nagy	PSI
Synthesis of soft materials with intrinsic concentration gradients by thermophoresis	D. Vigolo	ETHZ
Ion channels as gates for stimuli-responsive nanoreactors	M. Lomora	Uni Basel
Studying complex nanoparticle self-assembly at liquid interfaces using pendant drop tensiometry, microrheology and fluorescence correlation spectroscopy	A. Nelson	ETHZ
Controlling local packing and growth in C-S-H gels	K. Ioannidou	ETHZ
Janus magnetic liposomes for drug delivery	C. Monnier	Uni Fribourg
Emulsion-saliva interactions depending on protein conformation	D. Z. Gunes	Nestle
Interaction of model proteins with nanoscale materials – an ESR study	A. Sienkiewicz	EPFL

Conference Venue

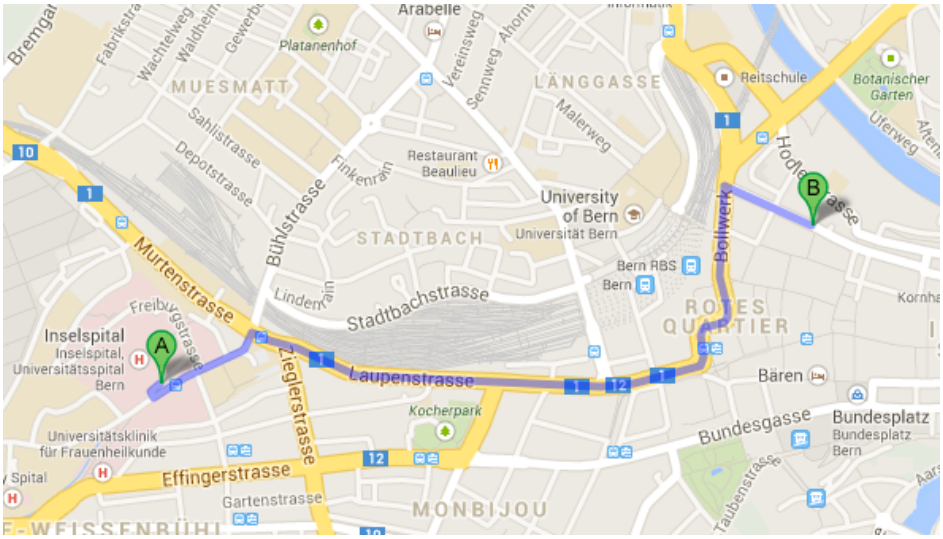
Shali-Haus-1, Inselspital, Bern





Get together: 18.30

Turnhalle Café-Bar
Speichergasse 4, 3011 Bern, Switzerland
+41 31 311 15 51 · turnhalle-bern.ch



Abstracts

Networks of patchy colloids on substrates

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[1] ETH Zürich, Zürich, Switzerland. [2] Centro de Física Teórica e Computacional, Universidade de Lisboa, Portugal.

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

METHODS: We introduced a novel stochastic scheme, based on nonequilibrium Monte Carlo methods. Considering low concentration in the bulk, only three processes can occur: collision with the surface; with the solvent; or with a pre-adsorbed colloid. For simplicity, collisions with the substrate always result in colloid adsorption. Collisions with the solvent are assumed Poisson processes. To account for particle-particle interaction we define an interaction range, on the surface of the colloid, around each patch. In the event of a collision with a pre-adsorbed colloid, if the binding is successful, the position of the landing particle is adjusted based on the patch-patch orientation; otherwise, an elastic collision occurs.

RESULTS: For the adsorption of three-patch colloids, the network density profile exhibits three distinct structural regimes: surface layer, liquid film, and interfacial region [1]; each one with interesting scaling properties. For the competitive adsorption of a mixture of three- and two-patch colloids, two mechanisms of mass transport are compared: diffusion and advection [3]. In the diffusive case, an optimal fraction is found that maximizes the density of the aggregate. By contrast, for advective transport, the density decreases monotonically with the fraction of two-patch colloids, in line with the behavior of the liquid density on the spinodal of the equilibrium phase diagram.

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

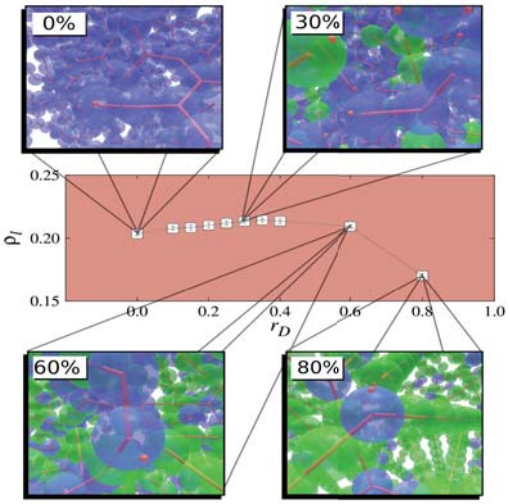

Fig. 1: Density of the liquid regime, for a diffusive transport as a function of the ratio of two-patch colloids.

DISCUSSION & CONCLUSIONS: This work reveals that, in the presence of a substrate and under nonequilibrium conditions, new self-organized patterns are obtained which differ from the thermodynamic optimal networks or equilibrium coexisting gels. We have shown that the kinetics of mass transport towards the substrate significantly affects the structure of the network of patchy particles. We have found that selective interaction between patches exhibit different structures than mixtures of patchy colloids.

REFERENCES: [1] C.S. Dias et al.; **2013**; *Phys. Rev. E;* 87:032308. [2] C.S. Dias et al.; **2013**; *Soft Matter;* 9:5616. [3] C.S. Dias et al.; **2013**; *Accepted for J. Chem. Phys.*

ACKNOWLEDGEMENTS: We acknowledge financial support from the Portuguese Foundation for Science and Technology under Contracts nos. EXCL/FIS-NAN/0083/2012,

PEst-OE/FIS/UI0618/2011,and
PTDC/FIS/098254/2008.

Modern microscopy techniques for biological studies Lifetime (FLIM) and super resolution (STORM) imaging of *Drosophila*

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In the current project we develop and implement improved strategies for the visualization of chemical synapses in the *Drosophila* adult brain, as well as other structures of interest. In order to overcome the diffraction limit of resolution, which hinders optical imaging of sub-micrometer features, we have implemented the Stochastic Optical Reconstruction Microscopy (STORM) [1]. One of our short-term goals is to quantify populations of pre-synaptic sites in young and adult flies. With the availability of different optical switches [2], we have also started imaging pre-and post-synaptic sites simultaneously, as well as the distribution of other proteins in order to validate the method in the drosophila model. In parallel to STROM we apply Two-Photon and fluorescence liftetime microscopy (FLIM) on the whole brain. We imaged the GFP expression genetically induced in glutamatergic neurons in the adult fly. The FLIM-analysis is performed using the "phasor approach" [3], a recent technique that circumvents the computational difficulties arising from multi-exponential fitting.

Reference:

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[4] R. A. Colyer, C. Lee and E. Gratton, A novel fluorescence lifetime imaging system that optimizes photon efficiency , Microscopy Research and Technique, Volume 71 Issue 3 pages 201–213, March 2008
[5] SEM image taken by Pete Splatt of Exeter Bioscience Bioimaging Department, drosophila brain scheme from Fischbach lab Institut für Biologie III der Albert-Ludwigs-Universität Freiburg

Emulsion-saliva interactions depending on protein conformation

J. S. Behra, D. Z. Gunes, T. J. Wooster, C. Loret

Nestlé Research Center, Lausanne, Switzerland

During food oral processing, interactions between food and saliva occur. Dresselhuis *et al.* (2008) have shown that saliva can induce coalescence of starch and protein stabilised emulsions, which is hypothetically related to an increase in creaminess perception of those emulsions. Coalescence of emulsions stabilised by starch-based emulsifiers has been explained by the activity of α-amylase, an enzyme present in saliva which degrades starch. To a smaller extent, coalescence has also been observed for non-starched emulsifiers like whey proteins. The aim of this study was to investigate emulsion-saliva interactions of two emulsions stabilised by proteins of different shapes: Na caseinate (linear) and whey proteins (globular).

Experiments were carried out with artificial saliva and different aqueous solutions containing some of its constituents in order to assess their respective roles in emulsion destabilisation. Emulsion-saliva interactions were investigated by visual observations, particle size distribution and creaming measurements.

For both proteins, Ccoalescence was only observed in the presence of "α-amylase" (porcine pancreatic amylase extract). It occurred earlier (before 30 min) for the Na caseinate stabilised emulsion than for the whey protein stabilised emulsion. The presence of a protease in the α-amylase source, confirmed by Size Exclusion Chromatography (SEC), could explain our results. The differences observed between coalescence speeds may be explained by differences in protein digestion which is related to their -conformation.

Regarding creaminess perception of coalesced emulsions, coalescence times are two orders of magnitude longer when compared to in-mouth process duration. This points to the need of conducting investigations in conditions closer to in-mouth conditions (human saliva, oral processing).

Switchable Transport across Modified Membrane Channel Proteins

C. Edlinger, C. Palivan, W. Meier and O. Fischer Onaca

University of Basel, Basel, Switzerland

INTRODUCTION: In recent years channel proteins have been used in nanoreactors for the admission of small molecules to the active site.[1] Of these the outer membrane protein F (OmpF) is one of the best studied examples. However, these channel proteins have no active diffusion control; active channels, are limited to the transport of specific molecules.[2] Modifying passive channel proteins such as OmpF enhances their functionality as tuneable gates for molecules.[3] We designed thus OmpF mutants featuring cysteines available in the pore region which we further modified with stimuli-responsive peptides containing a maleic imide terminal group. Bioconjugates of e.g. pH-sensitive oligomers and membrane channel proteins provide a facile route to novel, stimuli responsive membrane-gating devices. The blocking of the pore is reversible and the modular approach allows selecting the trigger, so that the system can be adjusted for specific applications as drug release or nanoreactors.

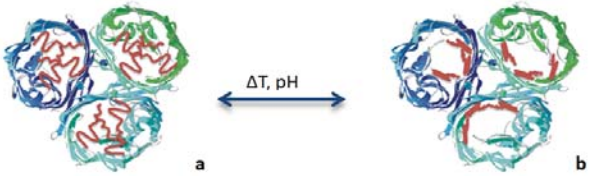

Fig. 1: Top-view of the OmpF-pore. The red parts represent the attached oligomers in the quelled state (closed pore: a) and in the collapsed/dehydrated form (open pore: b)

METHODS: The modified OmpF-mutants (bioconjugates) were inserted into liposomes' membranes for the evaluation of their functionality. The functionalized liposomes were obtained by film rehydration of DSPC/cholesterol film containing the bioconjugate. The diffusion through the pores was followed by using either (1) by fluorescence correlation spectroscopy (FCS) monitoring the release of sulforhodamin B (SRB) encapsulated in the liposomes, or (2) fluorescence spectroscopy to detect the activity of encapsulated horse radish peroxidase (HRP).

RESULTS: PH responsive peptides (water insoluble at pH 5.5, soluble above) were successfully linked to the OmpF mutant. The liposomes were produced so that the pores were initially in closed state. The pH triggered release of SRB was proved:

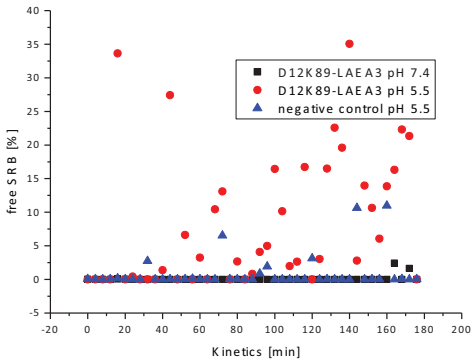

Fig. 2: FCS kinetic displaying the increase of the free dye population.

DISCUSSION & CONCLUSIONS:

The kinetic measurement revealed that the conjugate does not leak at pH 7.4 but looses up to 50% of the encapsulated SRB within 3h, at pH 5.5. Vesicles without OmpF did not leak and their stability was proven through size measurements using light scattering, tunnel electron microscopy (TEM) and diffusion time measurements in FCS.

We conclude that we functionalized successfully OmpF, produced thus a initially blocked pore and were able to open it through changing the pH.

Next steps include studies about the reversibility of the system and expand the system to other stimuli responsive oligomers.

REFERENCES: [1] C. Edlinger, X. Zhang, O. Fischer-Onaca, C.G. Palivan; **2013**; Polymer nanoreactors; *Encyclopedia of polymer science and technology*; Wiley. [2] Alberts B, Bray D, Lewis J, et al. 1994 Principles of Membrane Transport *Molecular Biology of the Cell*.; Garland Science. [3] S. Ihle, O. Onaca, B. Hauer, et al; **2011**; *Soft matter*; 7:532-539

ACKNOWLEDGEMENTS: The research has been financed by the SNF

Microscopic mechanism for the shear-thickening of non-Brownian suspensions

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H.Lombois-Burger[3], J.Cayer-Barrioz[4], HJ. Herrmann[2], ND. Spencer[1], L.Isa[5]
[1]LSST, ETH Zurich; [2]CPEM, ETH Zurich; [3]Lafarge LCR,St Quentin-Fallavier, France;
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Shear-thickening can lead to large-scale processing problems of dense pastes in a host of practical applications [1]. Despite extensive efforts to describe its microscopic origin [1-4], current explanations fail to address the mechanism behind the shear-thickening of dense granular pastes. In such systems networks of contacting particles can develop and transmit positive normal stresses [5]. Moreover, viscosity can suddenly diverge under flow (discontinuous shear-thickening [6-7]) with dramatic effects. Previous experiments have demonstrated that the features of the viscosity increase (slope, critical stress) can be controlled by tuning particle surface properties such as roughness[8] and/or by adsorbing polymers[9]. These findings suggest that inter-particle contacts play a crucial role in the macroscopic flow at high volume fractions and that a precise description of these contacts is essential to interpret the rheological behavior.

We propose a simple model, supported by contact-dynamics simulations as well as rheology and friction measurements, which links the transition from continuous to discontinuous shear-thickening in dense granular pastes to distinct lubrication regimes in the particle contacts. In particular we identify a local characteristic number (Sommerfeld number) that determines the transition from Newtonian to shear-thickening flows, and then show that the suspension's volume fraction and the boundary lubrication friction coefficient control the nature of the shear-thickening transition, both in simulations and experiments.

The generality and consistency of our data and of the proposed model sets a global framework in which the tribological (friction) and rheological properties of dense non-colloidal systems are intimately connected. This concept is expected to have an impact on a host of practical applications and relates fundamental issues such as flow localization [10] and minimum local shear rate of granular pastes [6].

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Interfacial activity of colloidally stable Janus-like silver nanoparticles by pendant drop tensiometry and direct deposition.

M.A.Fernández-Rodríguez[1], M.A.Rodríguez-Valverde[1], M.A.Cabrerizo-Vílchez[1], R.Hidalgo-Álvarez[1]

[1]*Biocolloid and Fluid Physics Group, Applied Physics Dept., Faculty of Sciences, University of Granada, 18071 Granada (Spain)*

INTRODUCTION: The interfacial activity of 100-nm Janus-like silver nanoparticles (AgJPs) can be enhanced with the use of different capping ligands. In this work, we explored the interfacial activity of 100 nm silver nanoparticles covered with two molecules with different hydrophilic character: 11-mercaptoundecanoic acid and 1-undecanthiol. The capping ligands spontaneously reorder at the water-air interface to form a Janus-like nanoparticle with two different faces with different hydrophilicity [1].

METHODS: We performed the compression isotherms at the water-air interface using the pendant drop technique [2]. For the particles deposition, we placed a tiny drop containing the Janus-like nanoparticles dispersed in methanol onto the initial pendant drop of MilliQ water. Once the methanol was completely evaporated, the pendant drop was grown up to a target volume and next, the interfacial/surface pressure of the shrinking pendant drop was monitored. We built each compression isotherm from different particle surface concentrations for a given initial drop area. Also it was measured the colloidal stability and the interfacial rheology of the Janus-like silver nanoparticles.

RESULTS:

The zeta potential of the AgJPs obtained using the Smoluchowski equation varies from -(8±6) mV (3.3 pH) to -(46±11) mV (10.8 pH). The results of surface pressure (Π) against the area per particle at the interface (A) form a piecewise compression isotherm. The Frumkin equation (Eq. 1) for a monolayer relates the surface pressure with the area per particle at the interface where k_B is the Boltzmann constant, T is the temperature, a is the particle geometrical area and α is the interaction constant [3]. The Frumkin equation was fitted to the experimental data in Fig. 1 before the collapse, resulting in the dashed black line in Fig. 1.

$$\Pi(A) = (k_B \cdot T/a) \cdot \ln(1/(1-a/A)-\alpha/A^2) \qquad (1)$$

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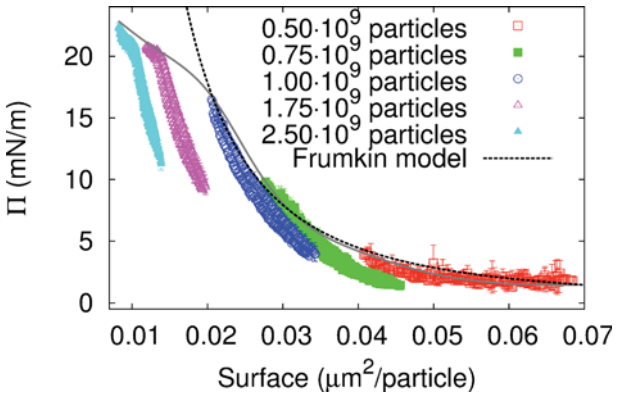

Fig. 1: Surface pressure against area per particle for different Janus-like silver nanoparticle number deposited at the water-air interface.

DISCUSSION & CONCLUSIONS: The nanoparticles revealed a significant interfacial activity like amphiphilic entities. The first term of the Frumkin equation is referred to the geometry of the system (i.e. how the particles are arranged at the interface) and the second term describes the interaction between the particles at the interface. The first term was negligible for our experimental data but the second term was fitted with a value of $\alpha=(1.15\pm0.08)\cdot10^{10}$ mN·m, highlighting the dominant effect of the lateral interactions between AgJPs at the water-air interface due to their electric charges.

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ACKNOWLEDGEMENTS: This study was supported by the ``Ministry of Science and Innovation'' (project MAT2011-23339) and by the ``Junta de Andalucía'' (projects P08-FQM-4325 and P10-FQM-5977). Authors thank to Dr. J.A. Holgado-Terriza, programmer of the software Dinaten used for surface tension measurements.

Transient formation of bcc crystal in suspensions of pNIPAM-based microgels

U. Gasser[1], J.-J. Lietor-Santos[3], A. Scotti[1], O. Bunk[2], A. Menzel[2], A. Fernandez-Nieves[3]

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[2] *Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI.*

[3] *School of Physics, Georgia Institute of Technology, Atlanta GA, 30332-0430, USA.*

INTRODUCTION: In suspensions of soft and deformable microgel particles, both the colloidal and the polymeric degrees of freedom are relevant for their phase behavior at high concentrations[1]. Recent simulation studies and theoretical work suggests that crystal structures different from those formed by hard spheres should form at high concentrations[2]. However, our experimental work[3] and the results of other groups[4] have shown that the crystal structure is comparable to that found in hard spheres.

METHODS: Here, we present data from a small-angle X-ray scattering (SAXS) study of crystal growth in a system of slightly charged microgels of poly(N-isopropylacrylamide) (pNIPAM) co-polymerized with acrylic acid (AAc). We study concentrated suspensions at fixed temperature and pH such that the particles are slightly charged and swollen. A series of samples covering the range of volume fractions with crystallization is used and the evolution of the samples with time is followed. The structure of the crystal is obtained from the observed Bragg peaks.

RESULTS: As in hard spheres, we find that random hexagonal close packed (rhcp)[5] crystal grows in all samples and slowly transforms towards the face centered cubic (fcc) lattice, which appears to be the equilibrium structure, as in hard spheres. However, at intermediate volume fractions, a body centered cubic (bcc) crystal phase appears, which is not stable and, therefore, disappears as the samples age.

DISCUSSION & CONCLUSIONS: Bcc crystals are also found in slightly charged hard spheres[6], however always at volume fractions below those where the fcc phase is the equilibrium structure. In contrast, for fuzzy particles wit a steric repulsion the bcc structure is not expected at low volume fractions but is predicted to appear in an intermediate range of volume fractions, between a loosely and a densely packed fcc phase[7]. In analogy to this model, we observe the transient bcc phase between bands of rhcp crystal that slowly converts to fcc. This suggests that our observations could be related to the predictions of the model for fuzzy particles[7]. The relevance of this model may be more pronounced for suspensions of softer microgels.

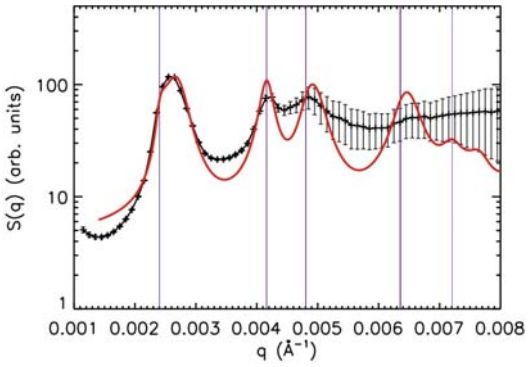

Fig. 1: Structure factor, S(q), obtained from SAXS of a sample with volume fraction 0.51. The red line shows the fit to the data obtained with the rhcp structure. The vertical lines show the Bragg peak positions for a hexagonal plane of particles.

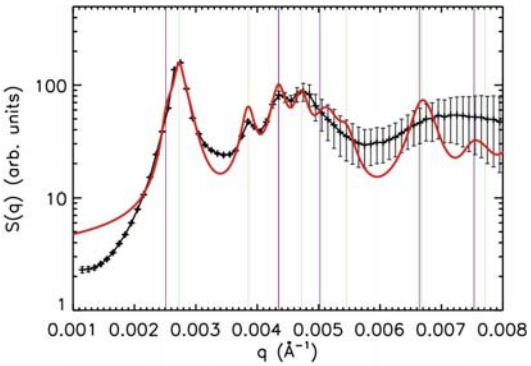

Fig. 2: Structure factor, S(q), obtained from SAXS of a sample with volume fraction 0.57. The red line shows the fit to the data obtained with both the rhcp and the bcc structure. The vertical lines show the Bragg peak positions for a hexagonal plane of particles (magenta) and the bcc lattice (green).

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Liquid-crystalline elastomer - nanoparticle hybrids with reversible switch of magnetic memory

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Abstract: Magnetic shape-memory materials are responsive materials with a strong influence of shape changes on the magnetic properties, and vice versa[1]. To induce magnetic anisotropy in easy-to-process systems, we propose a strategy exploiting shape anisotropy of ferrimagnetic nanoparticles (MNs) in organic-inorganic hybrids: A stimuli-responsive nanocomposite is synthesized that combines the actuation potential of liquid-crystalline elastomers (LCEs) with the anisotropic magnetic properties of ellipsoidal maghemite nanoparticles. Tensile strength analysis and X-ray scattering experiments are combined to establish detailed understanding of the microstructural coupling between the LCE network and the embedded magnetic core-shell ellipsoidal NPs[2]. Detailed studies on the magnetic properties demonstrate that the collective ensemble of individual NPs is responsible for the macroscopic magnetic features of the nanocomposite. The LCE nanocomposites allow for accurate control over the global orientation of the MNs and the macroscopic magnetic susceptibility. Thus, the resulting nanocomposite exhibits unique shape-memory features with magnetic information, which can be reversibly stored and erased via parameters typical of soft materials, such as high deformations, low stresses, and liquid-crystalline smectic-isotropic transition temperatures (Fig. 1). Independently of the particle loading, the shape-memory properties and the smectic phase of the LCEs are preserved. The obtained magnetic shape-memory material offers access to unique applications, including wireless actuators, switches and magnetic valves.

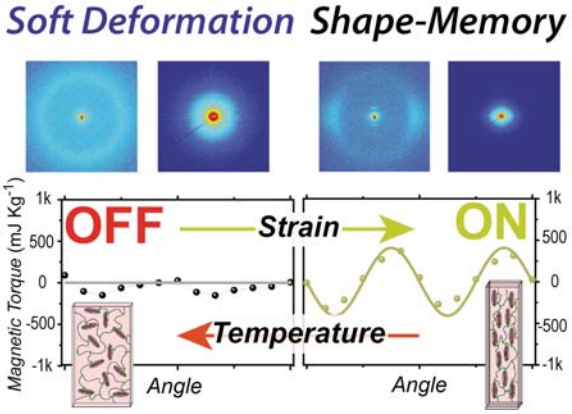

Fig. 1: In the OFF state, 2D X-ray scattering patterns and magnetic torque measurements prove the absence of orientation within the liquid-crystalline elastomer (LCE) nanocomposite. After an applied strain, the oriented ON state is reached and the LCE nanocomposite stores anisotropic magnetic information. This can be released upon heating due to the shape-memory features of the LCE.

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CONTROLLING LOCAL PACKING AND GROWTH IN C-S-H GELS

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INTRODUCTION: Mechanical and viscoelastic behavior of cement crucially depends on the Calcium-Silicate-Hydrate (C-S-H), the nanoscale "glue" of cement, and on the slow evolution (aging) of its local composition and morphology. C-S-H gel forms and densifies by precipitation of the nano-scale hydrates within a couple of hours [1-4]. Its microstructure is determined by the chemical conditions and the continuous particle precipitation that drives the system out of equilibrium. To examine the interplay between the effective particle interaction and the precipitation kinetics, we developed a coarse-grained colloidal model based on a combination of Monte Carlo and Molecular Dynamics numerical simulations.

DISCUSSION & RESULTS: Here, we present results on the evolution of C-S-H microstructure, for two attractive and repulsive effective interactions motivated by experimental measurements and the present theoretical understanding of C-S-H [5-7]. We discuss the microstructure and mechanical properties of out-of-equilibrium gels formed at different precipitation rates with respect to the phase diagram and the equilibrium properties of the model C-S-H. Our final aim is to rationalize how the precipitation process can be tuned to control the microstructure formation and hence, the mechanical performance of C-S-H.

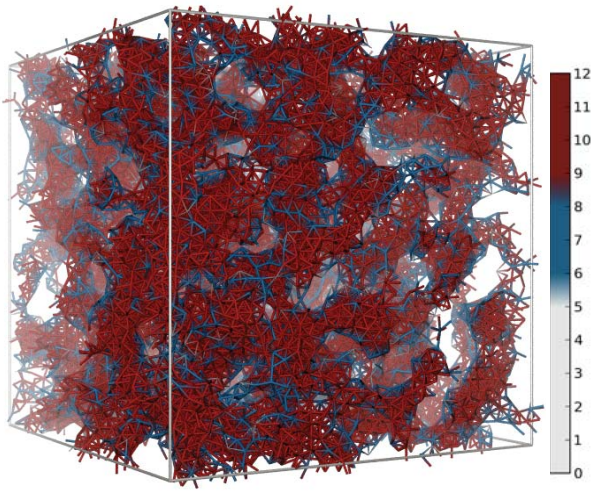

Fig. 1: Bond representation of the precipitated C-S-H gel, at volume fraction 0.26. The color code corresponds to the particle coordination number.

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Polymer membranes functionalized with aquaporins for applications in engineering and biology

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INTRODUCTION: Membrane proteins possess unique properties and by inserting them into artificial polymeric membranes, special protein-polymer hybrid materials can be designed to gain specific functions. Self-assembling amphiphilic block copolymers provide better chemical and mechanical stability comparing to lipids. The high permeability of cell lipid membranes is a disadvantage for protein studies and polymeric membranes provide better resolution for these kinds of experiments.

METHODS: Here, we use two artificial membrane systems, one based on the triblock copolymer polymethyloxazoline – polydimethyl-siloxane (PMOXA-PDMS-PMOXA), and one based on lipid cholesterol mixtures, to measure the P_{CO2} by the ^{18}O technique [1] for two different AQPs, hAqp1 and bacterial AqpZ. For water permeability studies, the stopped-flow technique was used to prove reconstitution of AqpZ and water transport, while rejecting ions [2].

RESULTS: We demonstrate, also in a physiological point of view, 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]. In addition, reconstituting membrane proteins in artificial triblock copolymer vesicles (2, 4) – 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.

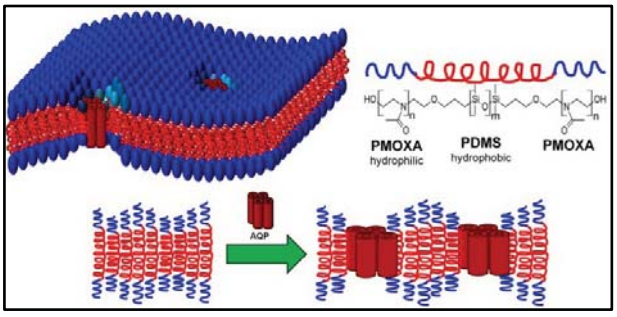

Fig. 1: Illustration of our polymeric membrane with reconstituted membrane proteins, and the triblock copolymer chemical formula.

DISCUSSION & CONCLUSIONS: Such artificial biomimetic membranes have great potential for applications in engineering and biology.

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Polymer-aptamer hybrid emulsion templating yields bio-responsive nanocapsules

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INTRODUCTION: Herein we describe the synthesis of a DNA-polymer, being the nucleotide sequence an aptamer selected in vitro to target specifically the immunoglobulin E (IgE) protein, an allergy biomarker. Subsequent to coupling to poly(2-alkyl-2-oxazoline) (PBOX) with N-protected amino acid side chains, the resulting amphiphilic DNA-polymer hybrid composed of the water soluble DNA fragment grafted to the hydrophobic polymer segment can be regarded as a high molecular weight analogue of a surfactant.

METHODS: In order to demonstrate that the copolymer-aptamer stabilizes efficiently sub-micrometer size oil-in-water and water-in-oil emulsions as well as to study the specific interaction between the capsules and the target, the following techniques were used: dynamic light scattering (DLS), microscopy and reflectometry.

RESULTS: The IgE-aptamer polymer hybrid has been successfully synthesized by solid phase synthesis according to well established chemistry routes. This macromolecule can be regarded as a high molecular weight analogue of a surfactant with the major advantage of being constituted of a bioinspired biocompatible synthetic polymer segment coupled to a biological stimulus-responsive nucleotide sequence. Results obtained from CLSM, AFM and reflectometry evidence that the aptamer remains functional subsequent to coupling to the polymer and engagement in the stabilization of the emulsion. The anti-IgE aptamer further retains its specificity. Further stabilization could be achieved by UV-irradiation of the cross-linkable pendent groups which were not modified with cysteine for subsequent grafting to the aptamer sequences. 11 vinyl pendant groups are therefore available in average per PBOX backbone for an eventual cross-linking polymerization step. Since this cross-linking step occurs at the oil water interface, the function of the aptamer is not affected.

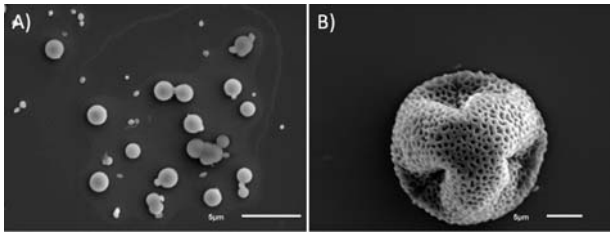

Fig. 1: Scanning electron micrographs of PBOX-aptamer capsules after cross-linking by irradiation with UV light A) Cross-linkage is performed subsequent to filtration B) large porous structures are observed when no extrusion is performed to reduce the size and fusion of the droplets might occur.

DISCUSSION & CONCLUSIONS: Coupling of the IgE aptamer to PBOX has been conducted through solid phase synthesis. The resulting amphiphilic copolymer-aptamer efficiently stabilizes oil-in-water and water-in-oil emulsions. Further stabilization could be demonstrated subsequent to an UV induced crosslinking polymerization step. Engagement of the aptamer in the emulsion stabilization does not hinder its specificity of binding to its target, which paves the wave for further developments of capsules for sustained and targeted delivery through the synergistic combination of site specific aptamer recognition and efficient encapsulation. The quantification of the aptamer binding kinetics and affinity to its target subsequent to polymer coupling and emulsion stabilization is currently under investigation.

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ACKNOWLEDGEMENTS: The Swiss National Science Foundation (SNSF PPOP2-128380) and the University of Geneva are greatly acknowledged for the financial support. We are thankful for the experimental support of Prof. Michal Borkovec, Dr. Bauer (Bioimaging platform from the University of Geneva), Prof. A. Zumbuehl (University of Fribourg), Dr. N. Gour, Dr. K. X. Ngo, Dr. J. Nixon, BSc F. Chevasson and MSc Mahshid Chekini.

A STUDY OF THE LIGAND EXCHANGE ON GOLD NANORODS LEADS TO A HYDROPHOBIC DRUG NANOCARRIER

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A plethora of nanostructures exist with differing surface chemistry and topology for applications ranging from novel biosensors to self-healing polymers, where their biological impact is often inferred from simple suspension exposures. However, it is often challenging to ensure adequate functionalization of these nanoparticles leading to uncertainty in the measured outcomes.

A prime example of how crucial this can be is the case of CTAB (Cetyl Trimethyl Ammonium Bromide) capped gold nanorods (GNRs) – CTAB is a cytotoxic surfactant necessary in the synthesis – where complete removal of the CTAB with a polymer has yet to be shown. We have investigated the detoxification of GNRs with PEG (Polyethylene glycol), generating a stability phase diagram allowing identification of regions where the GNRs were functionalized either at the end or the sides (Figure 1). This led to a two-step functionalization procedure, necessary to produce GNRs that were completely biocompatible, as tested in primary human blood monocyte-derived macrophages.[1]

Recently, we have extended the two-step procedure to another polymeric coating: Polyvinyl Alcohol (PVA). As previously developed, this was accomplished through a solvent exchange to desorb the CTAB while attaching the polymer – polyvinyl acetate (PVAc). This led to a system with two advantageous factors compared with simply using PEG. Firstly, the higher number of functional groups means a higher degree of ligands can be attached such as targeting moieties or fluorophores. Secondly, incomplete hydrolysis leads to a blocky coating of PVAc/PVA which allowed the encapsulation of a model hydrophobic drug molecule for triggered release (Figure 2). Finally, the PVA-GNRs were shown to be biocompatible using primary human blood monocyte-derived macrophages.

Both the above studies originated from an in depth characterization and study of the role of the stabilizing ligand – deemed crucial for both efficient functionalization and for ensuring biocompatibility.

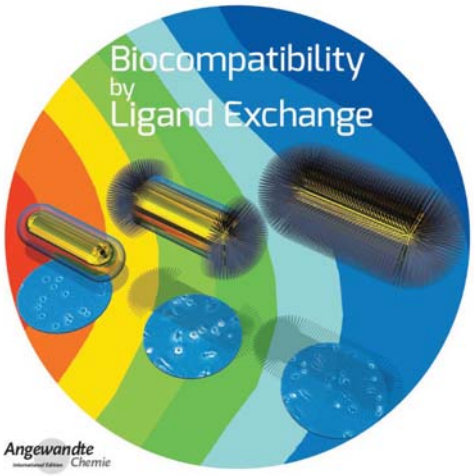

Fig. 1: Process of ligand exchange on gold nanorods: PEG first attaches at the end before near-complete coverage of the nanorod in a brush configuration imparting biocompatibility.

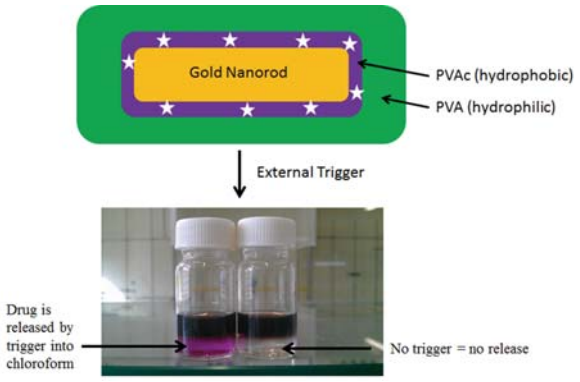

Fig. 2: Gold Nanorods coated with PVAc/PVA encapsulate a hydrophobic compound which is released upon an external trigger (here a small thiol molecule to displace the polymer).

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Application of Nanofibres for Biomedical Diagnostics and Therapy.

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Electrospinning of polymer fibres is one of the simplest and cheapest methods of producing nanomaterials. Electrospinning proceeds when a high enough electric field is applied to the liquid jet of a polymer solution. By action of the electrical stresses the jet is stretched by the bending instability and further on solidifies into an ultra thin fibre [1]. The possibility of using common biocompatible polymers, the presence of a numerous nanopores on the surface of the nanofibres is another key feature, facilitating their use in biomedical applications, such as drug delivery systems, nano-scaffolds for tissue engineering, and absorbable implants of skin or other tissues.

Nanofibres based on blood serum protein (BSA) were applied as a very permissive material for construction of fluorescent probes for bio-diagnostics [2]. Biocompatible nanofibres were also used to construct after-burn wound protective dressing successfully tested on the mouse skin. The nanofibrous mats were applied to prevent finger liaisons as well as to facilitate maintenance of a skin implants. Another research project deals with the use of electrospun nonwovens as a ureter or urinary bladder regenerative implants.

The successful application of electrospun nonwovens has been achieved recently as a dressing material for the prevention of excessive cicatrization after brain injury or spinal cord surgery [3]. Scaring is known as one of the major neurosurgery post-operative complications. It causes subsequent complications related to ingrowths of a connective tissue onto a spinal canal. Formation of an astroglial scar is another serious postoperative complication of the brain neurosurgery. The use of bio-absorbable isolative materials as anti-liaisons protection and as possible carrier for neuroprotective drugs delivery is expected to help solving such problems. The nanostructured material acts as anti-bacterial and anti-liaisons barrier whereas enabling transport of oxygen, nutrients and metabolites that positively influences healing process of the surgical wound. The insulating material is gradually degraded leaving behind lactic acid that does not adversely affects surrounding nervous tissue. The mats were applied as a barrier of a scar growth by placing them into an open spinal canal. They were applied in the course of the spinal laminectomy conducted on a rat model. The membrane was placed on the surface of the exposed spinal cord and covered with the surrounding it dura mater. The ultrastructural and immunehistochemical tests carried out after certain period of time have revealed lack of inflammation. The absence of astroglials or connective tissue scars that could be potentially dangerous to regeneration was also proven. Bone fragments of spine have been normally overgrown as a part of the healing process. The outcome of an experiment raises expectations for the development of a clinically approved barrier material used for prevention of post-operative complications commonly related to a scaring process following spinal surgeries.

The next step is to compose the biodegradable polymer with medical approvals to deliver drugs like: antioxidants – α-tocopherol and important in terms of regeneration of brain tissue NGF (Neural Growth Factor). Controlled release of these drugs provides the supply of the appropriate medicine dose over a period of 8 to 14 days. Construction of such system is a tedious experimental task. Hence, we take advantage of numerical simulation to construct a 3D finite element model which can help to optimize composition and geometrical structure of the nanofibres mat.

Acknowledgement
The support of NCBiR grant no 13008110 is acknowledged.

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Phospholipid Bicelles to Generate Magnetically Switchable Material

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With the goal of producing smart hydrogels, magnetically alignable bicelles were embedded into a gelatin matrix, generating a temperature responsive magnetically switchable structure. This results in nanometer-scaled switches operable by an external magnetic field for the anisotropy conferred by bicelles as functional ingredient. Bicelles are a self-assembly structure based on phospholipids with a disk-like shape. The bicelles studied in this work were composed of DMPC, cholesterol and DMPE-DTPA with complexed lanthanide ions (i.e. Tm^{3+} or Dy^{3+}) [1]. Magnetic alignment was caused by an anisotropic magnetic susceptibility $\Delta\chi$ of the phospholipids and the complexed lanthanide ions, leading to a preferred orientation of the molecular assembly parallel (with Tm^{3+}) or perpendicular (with Dy^{3+}) as shown in Figure 1 with birefringence and SANS measurements conducted in a magnetic field.

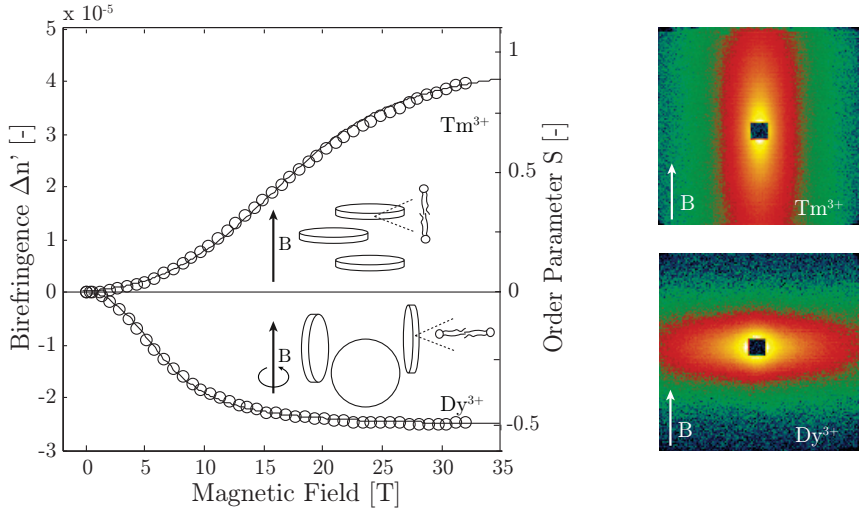

Figure 1: *Magnetically induced birefringence measurements (left) and SANS measurements in a magnetic field of 8 T (right) showing the different orientation direction of bicelles with Tm^{3+} and Dy^{3+} [2].*

The formation process of bicelles was investigated and optimized to yield a maximum magnetic alignment. The disk-like aggregates were preserved after embedding into gelatin and the magnetic orientation of the bicelles could be entirely fixed by gelation of the matrix. The resulting gel cubes showed an anisotropic transfer for electromagnetic waves, i.e. a different birefringence in all three orthogonal directions. Cycling through the melting point of gelatin set the bicellar alignment back to its isotropic state [3].

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Ion channels as gates for stimuli-responsive nanoreactors

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INTRODUCTION: The ability of ions to pass through cellular membranes is due to the various pore-forming peptides that serve to maintain the homeostasis, to preserve the stability of the internal cell's environment, or have a signalling role. In a bio-mimetic approach, we were interested to insert ion-channels such as gramicidin (gA) into the membranes of synthetic polymersomes, to design stimuli-responsive nanoreactors. Nanoreactors serve the dual role of simultaneously protecting sensitive enzymes from proteolytic attack, and allow them to act *in situ* [1]. Ion channels are used as "gates", which render the membrane permeable to substrates and products supporting *in situ* enzymatic reactions. The functional incorporation of gA enables to activate encapsulated enzymes precisely by changes of the environmental pH.

METHODS: Polymersomes were formed by the film rehydration method and their size and morphology were characterized by transmission electron microscopy (TEM), light scattering (LS) and fluorescence correlation spectroscopy (FCS). The pH sensitive dye, pyranine, was encapsulated in polymersome and the reconstitution of gramicidin into the polymer membrane was tested by a time driven fluorescence quenching approach [2]. This method proved to be useful for optimization of the choice of organic solvent used for the polypeptide dissolution, and to study the influence of various organic solvents on polymersome membrane. Stopped-flow spectroscopy was used to study the proton influx through the channels. In order to prove the concept and to optimize the conditions, gA was first inserted into the membrane of liposomes.

RESULTS: Polymersomes were formed by self-assembling of a diblock copolymer ($PDMS_{65}$-$PMOXA_{14}$). TEM images revealed spherical structures with a diameter of approximately 100 nm (*Figure 1 a*), in agreement with DLS and FCS results. By comparing the diffusion times of free dye (OregonGreen-488), OregonGreen-488 labelled gA (OregonGreen-488-gA) and of a mixture of labelled gA and polymersomes, a strong binding of gA to polymer membrane was observed. A gramicidin concentration of 142 nM and a mixture of solvents 2,2,2-trifluoroethanol: dimethylsulfoxide:ethanol (TFE:DMSO:EtOH) in a ratio 2:1:1 (*Figure 1 b*) was found to be optimal for insertion of gA channel proteins into polymeric membrane.

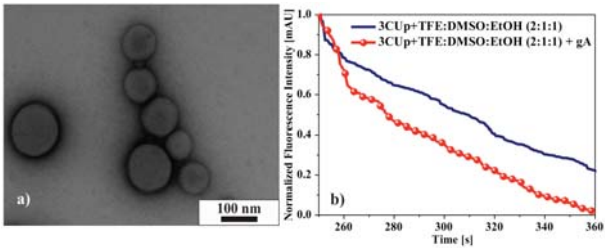

Fig. 1: a) TEM micrograph of pyranine-encapsulated polymersomes; b) Time-driven fluorescence quenching induced by proton diffusion through gA channels inserted inside the polymer membrane vesicles.

DISCUSSION & CONCLUSIONS: Polymeric vesicles were formed and gramicidin was successfully reconstituted into the polymer membrane of vesicles. The functional insertion of gramicidin represents the first step in the design of stimuli-responsive polymersomes. They will serve for encapsulation of a pH sensitive enzyme, able to amplify the environmental pH change. In addition, encapsulation of desired enzymes inside the aqueous cavity of the vesicle will serve to acquire specific signalling functions.

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A mechanical sensor to study movement at the nanoscale

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INTRODUCTION: The importance of the characterization of movement in biological samples ranges from the fields of biology and microbiology to pharmaceuticals and drug development. For instance, the movement of living systems can deliver useful information regarding the metabolism of the specimen under investigation and can be used to define their response to external stimuli.

METHODS: 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.

RESULTS: In this presentation I will show how nanomechanical sensors can be used to characterize the nano-sized fluctuations of biologically-interesting specimens. I will discuss the metabolism-related movements of different bacterial species, of yeasts and fungi and of plant and mammalian cells when exposed to various external stimuli. For instance I will show how bacteria react to antibiotics and how nanomechanical sensors can be used as extremely fast tools (minutes, compared to hours or days) to characterize bacterial resistances. Furthermore I will discuss how this system can be applied to the study of conformational changes in proteins and protein complexes.

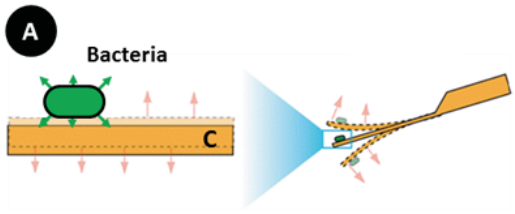

Fig. 1: The nanomotion sensor detects movements of samples deposited on its surface. Bacteria on the sensor's surface cause its fluctuation.

DISCUSSION & CONCLUSIONS: These studies have defined how this new diagnostic tool can be used to characterize biological samples and how this information can be used to understand better their metabolic pathways. The speed and sensitivity of the technique will have a massive impact, with applications in general and molecular biology, microbiology, drug development and medicine. Its versatility allows also foreseeing its possible future use to identify and characterize life in hostile environments.

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Interaction of model proteins with nanoscale materials – an ESR study

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INTRODUCTION: Evidence is growing that engineered nanoparticles (ENPs), due to their small size, unusual physical properties, like, *e.g.*, high surface area and high reactivity, might represent a real danger to human health and environment [1]. In particular, it has been demonstrated that ENPs can cross biological barriers relatively unimpeded [2]. In contrast, however, very little is known about the early stages of interactions of ENPs with physiological fluids. Recently, it has been emphasized that the early scenario of interactions of ENPs with physiological fluids might involve surface modification of ENPs by adsorption of lipids and proteins, thus leading to the formation of a bio-molecular layer, the so-called 'protein corona' [3]. It is worth noting that systematic quantitative studies of 'protein coronas' are still scarce. Thus, the goal of this study was to investigate the formation of protein deposits using a combination of site-directed spin-labeling (SDSL) and electron spin resonance (ESR) spectroscopy. SDSL takes advantage of easily measurable changes in molecular dynamics of an appropriately anchored spin-label (SL). Because SLs are sensitive to the molecular mobility and solvent accessibility of different fragments of the secondary structure of proteins, they can be used as reporters of protein structural changes. Such protein conformation changes are expected to occur due to the formation of 'protein coronas' - when intact protein molecules are exposed to waterborne ENPs.

METHODS: Human serum albumin (HSA) from Sigma Aldrich, Switzerland, was used as a model protein and was spin-labeled with 16-Doxyl-stearic acid spin-label (16-Doxyl), from Sigma Aldrich, to achieve the final concentration of the spin-labeled HSA (SL-HSA) of 0.5 mM. Then, SL-HSA was exposed to waterborne 200-nm gold nanoparticles (200-nm Au NPs), from Ted Pella Inc. The obtained solutions of SL-HSA and aqueous suspensions containing SL-HSA and Au NPs (SL-HSA / Au NPs) were characterized using electron spin resonance (ESR) and UV-VIS spectroscopy.

RESULTS: The ESR results obtained for solutions of SL-HSA and aqueous suspensions containing SL-HSA / Au NPs are summarized in Fig. 1. The characteristic broadening of the ESR spectrum shown in Fig. 1a points to a strong immobilization of 16-Doxyl SL in hydrophobic regions of HSA (Fig. 1a.). Moreover, the ESR spectrum of SL-HSA markedly changed after incubation of the protein with 200-nm Au NPs (Fig. 1b).

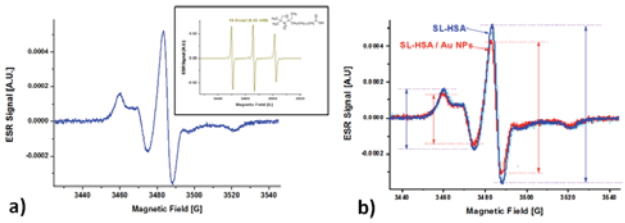

Fig. 1: Interaction of SL-HSA with 200-nm Au NPs: (a) the ESR spectrum of the SL-HSA; inset: the ESR spectrum of the free spin label, 16-Doxyl; (b) comparison of the ESR spectra of SL-HSA and SL-HSA incubated with 200 nm Au NPs.

DISCUSSION & CONCLUSIONS: The observed changes in ESR spectra (Fig. 1b) can be associated with protein conformation changes, which might occur upon formation of 'protein coronas' at the surface of Au NPs. These findings corroborated with alterations in UV-VIS spectra acquired for aqueous suspensions of Au NPs and SL-HSA / Au NPs. In particular, *ca.* 12-nm red-shift was observed for aqueous suspensions containing SL-HSA / Au NPs. Thus, our findings indicate that both ESR and UV-VIS followed and confirmed the attachment of HSA to 200-nm Au NPs and can be used to monitor the formation of 'protein-coronas' when proteins are brought into contact with ENPs .

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ACKNOWLEDGEMENTS: We gratefully acknowledge the financial support of the Scientific Exchange Program, Sciex-NMS[ch], through the project No. 12.112 "Nano-Crown".

Janus magnetic liposomes for drug delivery

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Delivering and releasing drugs at their target in a controlled fashion remains a key determinant of successful treatment and might contribute to reducing side effects.

By using liposomes as basic drug carriers and combining them with hydrophobic super-paramagnetic iron oxide nanoparticles (SPIONs), investigations in our lab have led to the development of nanoparticle-liposome hybrids with large nanoparticle clusters directly embedded within the membrane bilayer. SPIONs heat up when exposed to an alternating magnetic field, thus offering a potent release trigger as soon as the target is reached. Furthermore, these nanoparticles act as contrast agents in magnetic resonance imaging (MRI) and can thus additionally act as a tag for tracking down the present location of the injected medicine.

Unlike previous reports, our experimental procedure enables an incorporation of a very large quantity of nanoparticles in between the bilayer. These nanoparticles are clustered together at one pole of the vesicle, which in turn improves the resolution and quality of the MRI signal and release efficiency. Furthermore, these observations suggest that the elasticity of liposome membranes is greater than previously assumed and that structures far larger than presently supposed can be embedded between lipid bilayers. This consequently opens a notable area of applications in both biological and medical sciences alike.

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ACKNOWLEDGEMENTS: This work is supported by the Swiss National Science Foundation (126104, PP00P2-123373/1 and PP00P2133597/1), the Adolphe Merkle Foundation and the University of Fribourg.

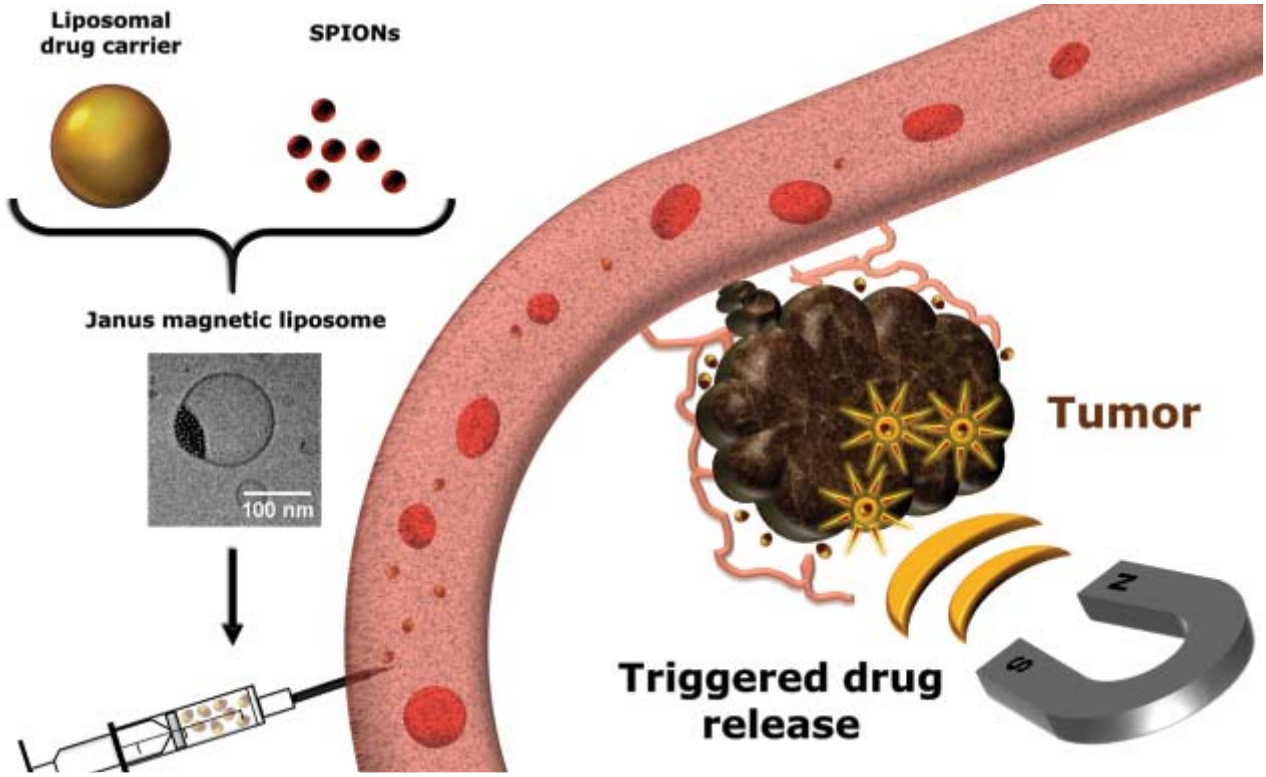

Figure 1: General concept overview: Janus magnetic liposomes can be used to precisely target pathological tissues (i.e. tumors). An alternating magnetic field can then be applied to release the encapsulated drug.

Reorganizations in the ultrastructure of the thylakoid membranes of *Chlamydomonas reinhardtii* cells upon state transitions

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In order to avoid unbalanced excitations of the two photosystems under variable light conditions, oxygenic photosynthetic organisms have evolved a rapid physiological adaptation mechanism by the aid of which the distribution of the absorbed light energy between the two photosystems can be regulated. The reversible processes, called the state transitions, in green algae and vascular plants, lead to the association and dis-association of the mobile antenna fraction of the major light harvesting complexes and, especially in *Chlamydomonas*, extensive supramolecular reorganizations (reviewed by Minagawa 2011 Biochim Biophys Acta 1807: 897). Electron microscopy data have indicated that the thylakoid membranes tend to be more stacked in State 1 and unstacked in State 2. However systematic quantitative studies and analysis on the Stt7 kinase mutant, which is incapable to perform state transition, have not been carried out.

In this work we studied state-transition related structural changes in the thylakoid membranes of *Chlamydomonas reinhardtii* cells using two independent non-invasive techniques, small angle neutron scattering (SANS) and circular dichroism (CD) spectroscopy. SANS carries spatially averaged information on the repeat distances (RDs) of periodically organized multilamellar membrane systems under physiologically relevant conditions. This technique has provided evidence for the occurrence of small (~1-2 nm) but well discernible light-induced reversible RD changes in different cyanobacterial and algal cells (Nagy et al. 2011 Biochem J 436: 225). CD spectroscopy carries information on the organization of the pigment systems at different levels of structural complexity. Of particular interest, the so-called psi type CD is sensitive both to the long-range order of the complexes and the stacking of thylakoid membranes. Light-induced reversible reorganizations have been reported earlier in different algal cells (for review, see Garab and Amerongen 2009 Photosynth Res 101: 135).

Our SANS and CD experiments, which were carried out with a time resolution of several minutes, provided clear evidence for the occurrence of major reversible membrane reorganizations during state transitions, which affected the periodicity of the membranes as well as the long-range order of the complexes in wild type cells. Significantly stronger periodicity, stacking and long-range order signals were observed in State 1 than in State 2, with the strongest signatures observed in the Stt7 mutant; this mutant, locked in State 1, was largely insensitive to the same treatments. Hence, these data provided clear experimental evidence for the occurrence of substantial ultrastructural changes during state transitions, which, as suggested by a comparison with fluorescence data, appear to occur only after persisting signals inducing the state transitions and to lag behind the fluorescence signatures - suggesting that the ultrastructural changes follow rather than precede the events directly associated with the (de)phosphorylation of membranes.

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

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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 different molecular weight and architecture PEG shells [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.

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 and to compare the effects of different PEG shells on the interfacial adsorption behaviour of the particles.

To further investigate the behaviour of the nanoparticles at the decane-water interface, the mechanical properties have been characterised via the tracking of probe particles with very different sizes. *Figure* 1 shows the setup used for microrheology. 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:

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

Fluorescence correlation spectroscopy (FCS), using quantum dots as tracers (5), was used to investigate the interface on the same length scale as the NPs.

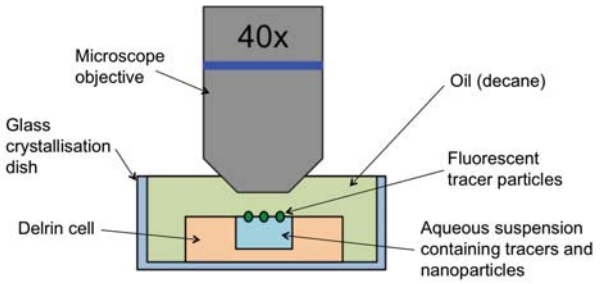

Fig. 1: Basic setup for microrheology using fluorescence microscopy.

RESULTS: PDT shows that particles with longer linear PEG chains show the highest surface activity and the fastest adsorption kinetics. Master curves have been created for the different particle types, demonstrating the concentration dependence of adsorption speed.

During microrheology the tracers still show diffusive behaviour at the interface upon adsorption of the NPs. Surprisingly, quantum dots also showed purely diffusive behaviour, with a progressive slowing down ascribed to NP adsorption. It was thus possible to follow the build-up of the NP monolayer with time, and to obtain master curves for the diffusion coefficient as a function of a concentration-dependent effective time, similar to the PDT master curves.

DISCUSSION & CONCLUSIONS: PDT shows a concentration-dependence of rate of NP adsorption to form a monolayer at the interface.

A micro-rheology 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. These results were then compared with those obtained using FCS in a similar method.

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A Label-free Serum Test Measuring overall Calcification Inhibition

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INTRODUCTION: Accelerated vascular and soft tissue calcification is a major problem in patients with chronic kidney disease (CKD). As serum is supersaturated with regard to calcium and phosphate, inhibitors of calcification critically determine pathological calcification[1]. Therefore, an assay measuring the overall calcification inhibitory capacity in blood would be helpful to make informed therapy decisions.

METHODS: We developed a label-free assay to quantify calcification-inhibitory properties contained in serum[2]. The assay measures the formation of protein-mineral aggregates in real time in a multi-well format.

RESULTS: Using this assay, we demonstrate that in the presence of high amounts of calcium and phosphate, primary calciprotein particles (CPP) are formed in serum. Primary CPP are spherical colloidal particles of 50-100 nm diameter. Subsequently, these primary CPP undergo spontaneous transition to spindle shaped secondary CPPs. Primary CPP are mainly comprised of fetuin-A and albumin, as demonstrated by protein gel and Western blot analyses. The size of the resulting secondary CPP is regulated mainly by two serum-inherent proteins: fetuin-A and albumin, with albumin synergistically substituting low fetuin-A concentrations. We furthermore demonstrate that the transition step is delayed in the presence of magnesium, and accelerated in the presence of phosphate.
Applying the test to biological samples, we found that both the sera of mice deficient in fetuin-A, and the sera of patients on hemodialysis have reduced intrinsic properties to inhibit calci!cation.

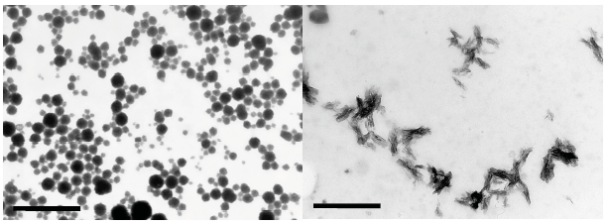

Fig. 1: Transmission electron microscopy images of primary (left) and secondary (right) calciprotein particles. Bar = 500 nm. Image from Ref. 2.

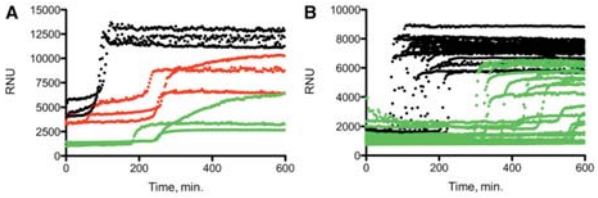

Fig. 2: (A) Nephelometry assay using sera from adult (10-16 months-old) non-calcifying wildtype DBA/2 mice (green), non-calcifying heterozygous fetuin-A$^{+/-}$ knockout mice having half-normal serum fetuin-A (red), and from heavily calcifying fetuin-A-deficient homozygous fetuin-A$^{-/-}$ knockout mice (black); (B) nephelometry assay with sera from 20 hemodialysis patients (black), and 20 healthy volunteers (green). Image from Ref. 2.

DISCUSSION & CONCLUSIONS: We have developed a novel test to assess the overall calcification inhibitory capacity of serum. This test may have an important role in the identification and specific treatment of calcification-prone CKD patients.

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[2]A. Pasch et al.; **2012**; *J Am Soc Nephrol;* 23(10):1744-52

Simulations of Breakage and Restructuring of Colloidal Aggregates in the Presence of Repulsive Interactions

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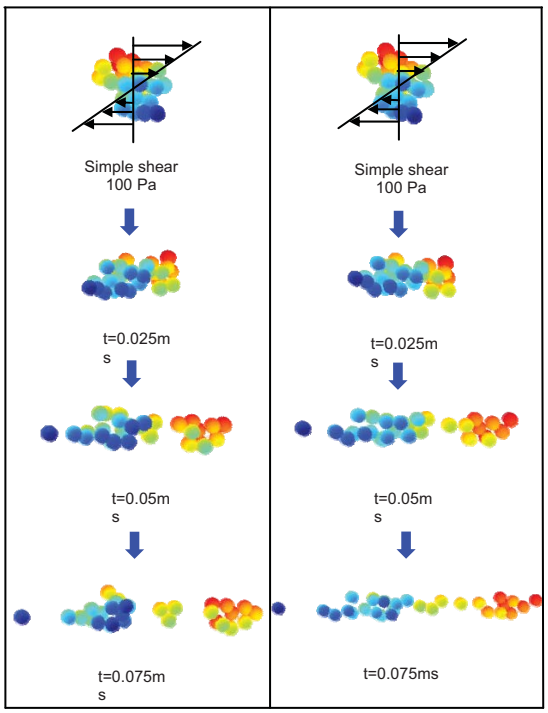
INTRODUCTION: Coagulation of colloidal suspensions is often performed for industrial applications in the presence of shear forces. But the process of how fractal clusters are broken by shear forces is difficult to model and to make predictions about. Aim of this work is to use Stokesian Dynamic (SD) simulations to quantify the dynamic behavior of fractal colloidal clusters in the presence of shear forces and electrostatic repulsive forces.

METHODS: The breakage and restructuring of colloidal aggregates under shear were analyzed by means of Stokesian Dynamics simulation. A library of clusters made of identical spherical particles covering a broad range of masses and fractal dimension values (from 1.8 to 3) have been generated by means of a combination of several Monte-Carlo methods. The hydrodynamic interactions among the particles have been accounted for by Stokesian Dynamics. DLVO theory has been used to describe the interparticle interactions, while contact forces, described by means of discrete element method, have been included to provide the clusters with realistic structural rigidity. The aggregates breakage process was investigated by exposing them into a well-defined shear forces, generated under both simple shear conditions and elongational flow. To investigate the evolution of aggregate size and morphology, respectively, the mean radius of gyration and the cluster fractal dimension were monitored during the breakup process[1]. Considerable attention has been given to understand the effect of electrostatic repulsive interactions on both the breakage rate and restructuring of the aggregates.

RESULTS: The breakage of a cluster with 30 particles and fractal dimension 2.5 under external shear stress 100Pa was shown in Fig.1. By applying different DLVO repulsion force, it is indicated that the clusters tend to break into large fragments if the electrostatic force is low (Fig.1a), while they break into smaller fragments in the high electrostatic repulsive forces was presented (Fig.1b).



(a) *(b)*

Fig.1 Cluster break under different DLVO conditions (a) particle radius = 1μm, surface potential = 30mV, bulk ionic concentration = 0.01mol/m^3 ; (b) particle radius = 1μm, surface potential = 60mV, bulk ionic concentration = 10mol/m^3 .

DISCUSSION & CONCLUSIONS: Stokesian Dynamics simulations combined with DLVO theory was used to simulate the breakage of clusters under simple shear conditions. The influence of surface potential, shear stress and ionic strength was investigated. It has been found that the presence of repulsive interactions enhances the breakage rate of clusters. The cluster breakage rate increases as both the ionic strength and the surface electrostatic potential increase.

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Pumping of blood in capillary networks

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INTRODUCTION: Blood viscosity has an important implication for many physiological processes and its alternation can lead to several pathological conditions[1]. Blood viscosity changes with the diameter of the vessels. In small capillaries blood undergoes shear thickening and shear thinning effect [2]. Hematocrit drops in such a case to the about 10% . The elasticity of the cells can be taken to account as well as the interactions between cells. We have built a micro device, which utilize this phenomenon. It is a microfluidic chip where the size of the channel is of the size: 20x5 μm. The shape of the channels (wavy form) increase naturally occurring perturbation in blood and lead to pumping of the blood without the requirements of additional external pumping. We have performed experiments and have tracked RBC on the microchip. By analyzing the velocity of RBC we could validate the shear thinning of the blood. This effect and method can be implemented in various devices, which are requiring effective blood pumping.

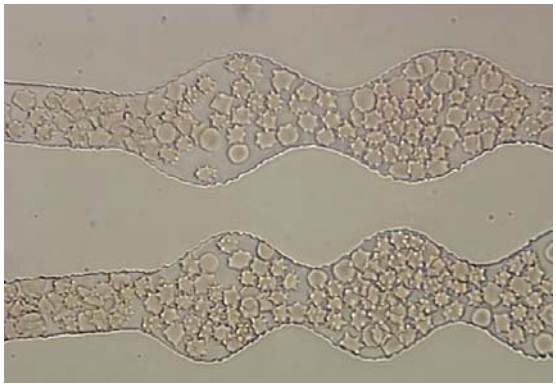

Fig. 1: Blood sample from the blood bank in the non-symmetric microchannel.

METHODS: We have performed experiments in a microfluidic chip using blood samples from the blood bank (Fig. 1). The RBC flow in microchip was investigated under the microscope The movies were recorded with a camera with a frequency of 25fps. The magnification used varies, but for result presentation we have shown pictures with 400x and 1000x magnification. The microchip was connected to the syringe pump by tube of 1.2mm diameter. The blood sample was obtained from the blood bank. Studies were performed over few days and for each case the new sample from the blood bank was taken. The blood sample from the blood bank was prepared in SAGM solution. The RBC concentrate was than dissolved in saline solution to obtain 10% hematocrit, which is common value for capillary flow. To avoid blood coagulation sodium citrate was added.

The microchips were designed using Comsol Multiphysics software and performing laminar flow simulations. Next data were translated to Autocad. The file was send to Stanford University Foundry and there the mask and microchip were manufactured in PDMS.

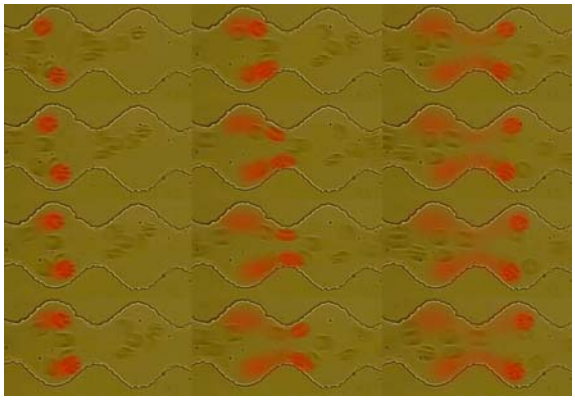

Fig. 2: Flow patter for the low hematocrit. Timeline is from top to bottom and from left to right.

RESULTS: We have performed several experiments for various frequencies of the channels, hematocrit level and non-symmetry of the channel (Fig. 2). The low hematocrit level leads to the flow characteristic similar to laminar creep flow [3]. The medium hematocrit shows interesting cell dynamics patters. The interaction of the RBC leads to the pumping effects. RBC paths express mixing patters.

DISCUSSION & CONCLUSIONS: The channel design supports the geometry induced pumping. The effect can be used to supply microfluidics devices with blood in a steady way without external pumping sources.

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[3] Feng at al.; **1995**; *J. Fluid Mech.;* 303:83-102.

Bacterial hydrophobicity and biofilm formation at water-oil interfaces

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INTRODUCTION: Bacterial adsorption to interfaces is a key factor in biofilm formation. One major limitation is the accurate measurement of bacterial cell adhesion to hydrophobic interfaces as well as the biofilm formation and development. With this study, we present a method which can measure both, bacterial attachment and biofilm growth over time at liquid-liquid interfaces.

METHODS: Five model bacteria (*Pseudomonas putida KT2442* and *W2, Salmonella typhimurium, Escherichia coli,* and *Bacillus subtilis*) were adsorbed at the water-oil interface either in their non-growing or growing state to observe bacterial attachment and biofilm formation. The initial bacterial attachment was measured through interfacial rheology and pendant drop tensiometry. Additionally, electrophoretic mobility measurements and bacterial adhesion to hydrocarbons (BATH) tests were performed. To validate interfacial rheology and tensiometry measurements, bacterial attachment and biofilm formation utilizing both confocal scanning laser microscopy and light microscopy was monitored.

RESULTS & DISCUSSION: Bacterial adsorption could be observed through a rise in interfacial elasticity and this can be correlated with the amount of bacteria adsorbed at the interface. *P. putida* strains have a high affinity towards oil and thus form an elastic network. *E.coli* on the other hand were not able to form an elastic network as only a few cells adsorbed at the interface (see Figure 1 A). Whereas *P. putida*, presented a strong and thick biofilm formation, *E.coli* biofilm architecture did not lead to high interfacial elasticity values (see Figure 1 B).

CONCLUSIONS: We were able to observe the initial kinetics of bacterial attachment and the transient biofilm formation at the water-oil interface through interfacial rheology and tensiometry. Using interfacial rheology will allow us to more accurately understand the dynamics of biofilm formation under a range of different conditions and can provide insight into factors which determine when and how biofilms are formed.

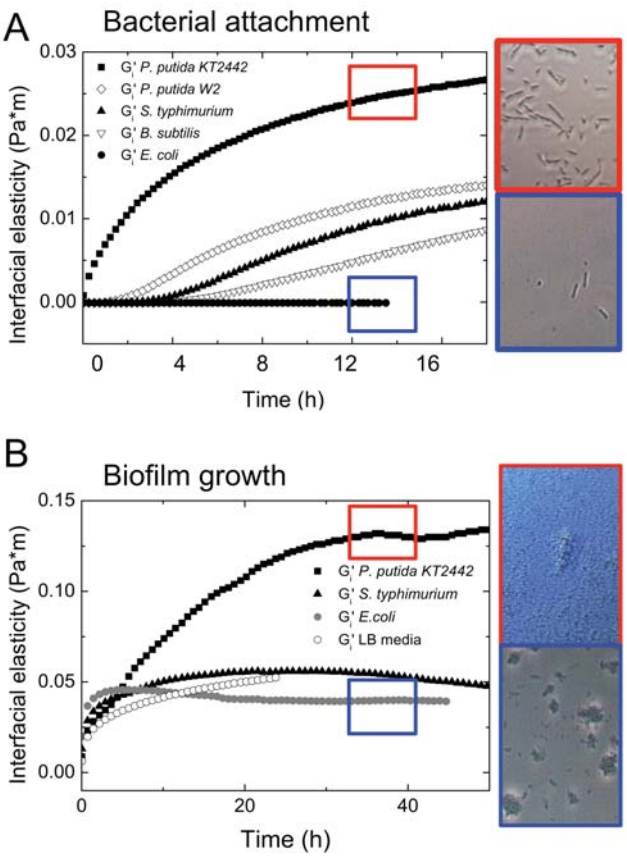

Fig. 1: A: Interfacial rheological time sweep of bacteria adsorbed at the mineral oil-water interface. B: Interfacial rheological time sweep of bacteria adsorbed and growing at the mineral oil-water interface. Microscopic images of the water-oil interface of E. coli and P. putida KT2442 during bacterial attachment and biofilm growth are shown on the right side.

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Liquid-Crystalline Elastomer Micropillar Array for Haptic Actuation

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INTRODUCTION: The combination of the liquid crystal anisotropy and the entropy elasticity of polymer networks results in materials with unique physical properties: liquid-crystalline elastomers (LCEs).[1]

Microactuators can be designed based on LCEs, opening new possibilities for microengineering. Previous works on using LCEs for the development of the Microsystem Technology have been performed by using low glass transition temperature networks based on siloxane chemistry.[2,3]

We present a successful nematic side-chain liquid-crystalline elastomer micropillar array which expands in the direction of the applied orientation when the isotropic temperature is reached.[4] This pushing behavior of the micropillars is related to the changes from the two-dimensional prolate polydomain conformation (nematic state) to the spherical conformation (isotropic state) of the polymer backbone.

RESULTS & DISCUSSION: In the nematic state, the LCE micropillars have average dimensions of 3.00 mm in height and 2.46 mm in diameter. After heating the LCE array to the isotropic phase, the average dimensions of the micropillars changed to 3.63 mm in height and 2.10 mm in diameter. (Fig. 1)

The mechanical actuation was analyzed, by measuring the forces exerted by the micropillar during expansion upon heating and contraction upon cooling. The force was measured as function of time using a dynamometer, while heating the bottom part of the LCE micropillar array. The maximum measured force was F = 20 mN at the set temperature of T_{set} = 90 ºC. The time needed to reach this maximum force was around t = 2 min, and showed full reversibility and repeatability upon cooling of the LCE micropillar array.

The values for the change in height (Δz = 630 μm), force (F = 20 mN), and stress (σ_t = 5.6 kPa), together with the processability and tunability of the chemistry in terms of mechanical and thermal actuation, make these LCE optimal materials for haptic applications, and their use as Braille displays. A Braille blister will require micropillars of 1.0-1.2 mm in diameter, a minimum change in height of 300 μm, and minimum forces of 15-30 mN, together with short switching times below the second scale. The energy efficiency and time responsiveness need to be investigated further.

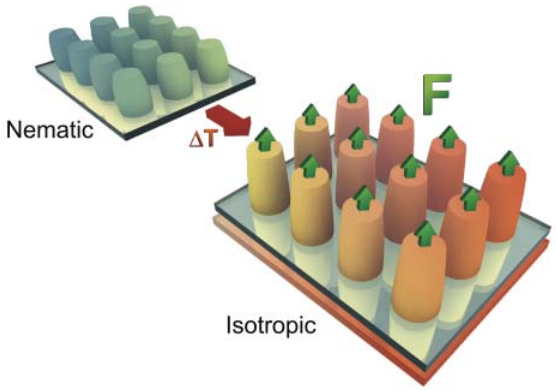

Fig. 1: Micropushers obtained by uniaxial compression with actuation temperatures around 55 ºC.

CONCLUSIONS: A new LCE micropillar array with two-dimensional prolate polydomain conformation of the polymer backbone and the mesogens has been successfully synthesized. This new concept of the orientation of silicone-based LCE systems by uniaxial compression (biaxial orientation) allows for the obtaining of micropushers, with actuation temperatures around 55 ºC. The two-dimensional prolate polydomain conformation of the LCE micropillars was confirmed by swelling, polarized optical microscopy and X-ray experiments, where the anisotropic swelling value above the unit and the planar distribution of the prolate polymer backbone and nematogens were observed.

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Thermo-Responsive Peptide-Based Triblock Copolymer Hydrogels

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INTRODUCTION: Hydrogels are physically and/or chemically crosslinked three-dimensional polymeric networks which absorb large amounts of water. This kind of materials have gained a great interest during the last few decades due to their excellent biocompatibility and capability to absorb and release molecules during the swelling-unswelling processes.[1]

Stimuli-responsive hydrogels are very appealing systems because of their reversibility when sol-gel transition or volume phase transition are present in response to the external physical or chemical stimuli, such as pH, temperature, ionic strength, magnetic field, and light.[2]

A combination of a polypeptide with a thermo-responsive polymer is herein proposed, which could offer new possibilities for the development of novel hydrogels that simultaneously exhibit the properties of both components. Further modification and physical crosslinking of the polypeptide block allowed obtaining the desired hydrogel networks, whose main physical properties are also investigated in the present work.[3]

RESULTS & DISCUSSION: A series of novel thermo-responsive peptide-based triblock copolymers, (PLGA-*b*-PNIPAM-*b*-PLGA) were successfully synthesized via ring opening polymerization. These triblock copolymers form a physically crosslinked networks after complexation with a diamino-terminated PEO in organic solvent through acid-base proton transfer and successive ionic-bonding. The secondary structure of the peptide block, before and after complexation, was confirmed by circular dichroism and SAXS measurements, showing an α-helix conformation of the PLGA segments. Swelling experiments on the ionic-bonded networks showed that the water uptake process strongly depends on the temperature and relative humidity conditions. Thus, higher humidity and temperatures below the lower critical solubility temperature (LCST) of the PNIPAM block increase the absorbed quantity of water into the network. These swollen ionic complexes contract and reject water anisotropically when these thermo-responsive peptide-based hydrogels are heated up above their LCST (Fig. 1).

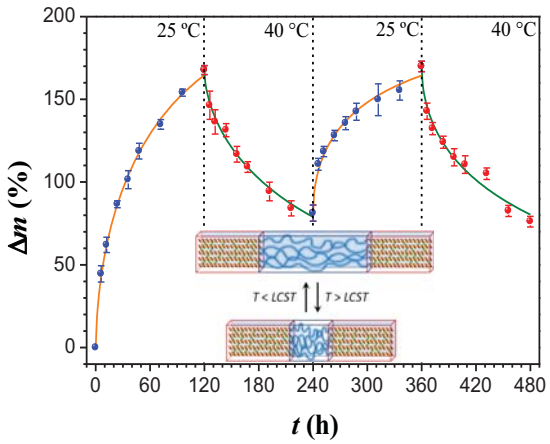

Fig. 1: Swelling and deswelling cycles of thermo-responsive peptide-based triblock copolymer in water atmosphere at 25 ºC and 40 °C.

CONCLUSIONS: A new series of rod-coil-rod peptide-based triblock copolymers which contain a thermal-responsive coil block have been synthesized and complexes were obtained by acid-base proton transfer between the carboxylic acid groups from the peptide block and the amine groups from a hydrophilic polyether crosslinker. The resulting ionic complexes swell water from the atmosphere and behave as thermal-responsive hydrogels. The equilibrium swelling ratio of these hydrogels increases with increasing equilibrium relative humidity and decreasing temperature. Moreover, kinetics of the swelling process are faster at low equilibrium relative humidity and at high temperatures. Given the biocompatibility of all components and the temperature responsiveness of the system, which allows iterative and fast sorption-desorption cycles of water, these peptide-based hydrogels show promise in biotechnological and biomedical applications, as tissue engineering and injectable materials for drug delivery.

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Crowding and ordering in the adsorption of nanoparticles at liquid-liquid interfaces

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Self-assembly of nano-particles at liquid-liquid interfaces opens new ways of tuning material properties at the nano-scale.

With the goal of choosing the right nanoparticle/liquids systems, many efforts are currently at controlling the process at the level of the single particle. Nevertheless recent experiments have monitored the adsorption process via the change, as the adsorption proceeds, of the effective surface tension of a particle-laden interface and have shown that, upon increasing the bulk concentration of nanoparticles, the adsorption can unexpectedly slow down reaching a plateau followed by further adsopption at later times [1]. These observations suggest that cooperative and slow dynamical processes due to particle crowding at the interface might affect the adsorption and change the properties of the final assembly. In feedback with the experiments, we have designed a model and a numerical study to investigate this problem.

The nanoparticles are modeled as repulsive soft-spheres and for the adsorption-desorption process we use a Grand Canonical Monte Carlo scheme, whereas the particle dynamics at the interface is investigated via Molecular Dynamics.

In the model we can control the rate of adsorption, corresponding to different particle bulk concentrations in the experiments, and investigate how it affects the development of the interface. The effective surface tension obtained from the simulations displays indeed the same behavior observed in experiments for high adsorption rate. Our results show that the intermediate plateau is due to a progressive jamming of the interface that is able to arrest the adsorption. Our analysis of particle rearrangements shows how local ordering processes can improve particle packing at the interface and eventually allow for the additional adsorption events at later times.

The evolution of local ordering and packing defects is also controlled by the adsorption rate, which appears therefore as a key ingredient to design the self-assembly and the properties of the interface.

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Effect of size polydispersity on the phase behaviour of soft microgel suspensions

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INTRODUCTION: For hard spheres, size-polydispersity is a limiting factor for crystallization. No hard sphere crystals form at polydispersities higher than 12%. In contrast, 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[1].

METHODS: We systematically study the role of polydispersity in suspensions of fully swollen poly(N-isopropylacrylamide) (pNIPAM) microgel particles. The thermodynamic quantity that rules the phase behavior is the genarlized volume fraction ζ. For all our samples the phase behaviour is studied by using series of 10 - 15 samples which cover the ζ range of interest. 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%, Fig 1.

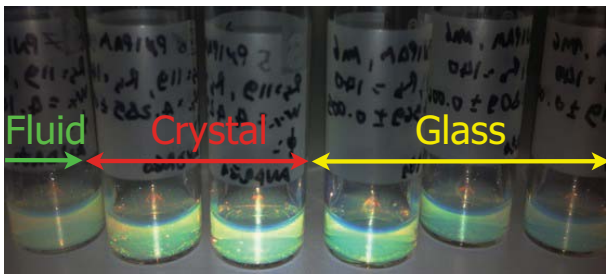

Fig. 1 Sample with a size-polydispersity of 13.5 that shows crystals

RESULTS: We have determined the crystal structure and lattice constant using small-angle X-ray scattering with crystalline samples. The measured lattice constants are consistent with crystals formed of the small particles, suggesting that the large particles adapt to fit into the lattice. Crystals are observed in samples with a number fraction of big particles as high as 8%. Using SANS with contrast matching of the small particles, we have proven that the big particles shrink in concentrated suspension. We have blended a majority of small deuterated particles with 10.5% of big protonated ones. Due to the different scattering length of Hydrogen and Deuterium, an appropiate mixture of heavy water and normal water, suppresses the contribution to the scattering due to the small particles and we have access to the form factor of the big particles even in very concentrated samples. We see that the radii of the big particles decrease from 192 nm to 146 nm with increasing concentration of small particles, Fig 2.

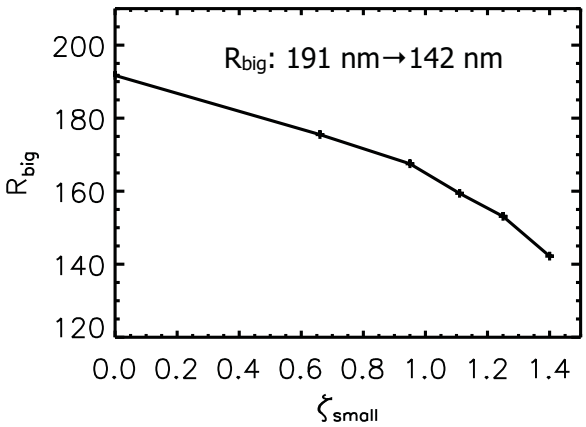

Fig. 2 Variation of the radius of the big particles with the increasing of the concentration of small particles

DISCUSSION & CONCLUSIONS: Our results show that the role of size-polydispersity in soft and deformable microgel suspensions fundamentally differs from that in hard spheres.

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Laccase encapsulating polymersomes for catalysed biotransformation

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INTRODUCTION: Laccases represent a class of enzymes with various industrial and biotechnological applications due to their ability to oxidize lignin compounds and persistent environmental pollutants.[1] As their applications require the ability of the laccase to maintain activity in aggressive environmental conditions (presence of various degrading agents), its protection is mandatory. In order to increase the stability of laccase and to protect the enzyme from inhibitors and proteolytic attack, we propose an alternative route: enzyme encapsulation in polymer vesicles [2], specifically designed to serve as compartments. *In situ* active laccase (Lac) will serve as active component for the design of nanoreactors. In order to reduce the complexity of the nanoreactor preparation, we chose to assemble polymersomes from block copolymers that are highly permeable for oxygen and for reactive oxygen species. Thus, the laccase would be protected by encapsulation within a polymersome, while still being accessible for its key substrate, oxygen. ROS produced by the enzyme will leave the nanoreactor, and react with other substrates in a non-enzymatic radical reaction outside polymersomes. Poly(*N*-vinylpyrrolidone)-poly(dimethylsiloxane) (PDMS-PNVP) are copolymers with exceptional high permeability for oxygen and ROS.

METHODS: The dimensions of the extruded vesicles were determined by dynamic and static light scattering (DLS, SLS). The morphology as well the size of the formed polymersomes was characterized by transmission electron microscopy (TEM) on a Philips EM400 electron microscope. UV-Vis spectroscopy was measured on a Specord 210 plus spectrometer (Analytik Jena, Germany). Gel permeation chromatography (GPC) was used in order to determine the polymers' number average molecular weight M_n and polydispersity index (PDI). ^{1}H-NMR spectra were recorded on a Bruker DPX-400 spectrometer operated at 400.140 MHz in $CDCl_3$ and processed with MestReNova software. EPR measurements were performed on a Bruker CW EPR Elexsys-500 spectrometer. EPR spectra were simulated using the WINSIM (NIEHS/NIH) simulation package.

RESULTS: PDMS-PNVP copolymers were synthesized according with the method described in the literature [3]. Considering that for our application the formation of polymersomes was mandatory, we chose to synthesize five different copolymers starting from two different sizes of the siloxane block (degree of polymerization of 17 and 37, respectively) and small hydrophilic blocks. The molar ratio in of vinyl and siloxane units was set to be between 0.5 and 1. Five different PDMS-PNVP polymers were prepared in order to determine those that are able to self-assemble into vesicles. All the 5 PDMS-PNVP copolymers were able to self-assemble in vesicles and to encapsulate Lac in polymersomes with diameters around 200 nm (TEM) (Figure 1), Rg (ranging from 70-120 nm) and ratio R_g/R_h (ρ-parameter) around 0.9 indicating the formation of hollow spheres. Moreover, Lac encapsulating polymersomes were able to maintain their activity (ABTS test) after encapsulation and to protect the encapsulating enzyme toward the degradation in the presence of proteinase K and sodium azide (known as common inhibiting agent).

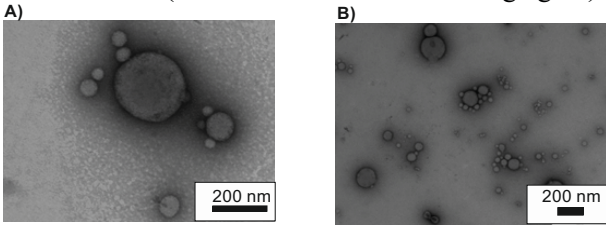

Fig. 1: TEM micrographs of empty and Lac encapsulating PDMS-PNVP polymersomes (A) PDMS-PNVP1, (B) PDMS-PNVP1-Lac).

DISCUSSION & CONCLUSIONS: PDMS-PNVP triblock copolymers can self-assemble into polymersomes in acidic conditions and are able to encapsulate laccase under retention of the enzyme's activity. The polymersomes act as nanoreactors for the biocatalyst, as they are permeable for the Lac substrate oxygen. Moreover, the polymersomes protected the encapsulated laccase against degradation or inhibition, demonstrated by incubation of the nanoreactors with proteinase K and sodium azide. PDMS-PNVP nanoreactors can be of interest for cosmetic applications, and for biomedical applications.

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ARTIFICIAL COMPACTION AND DECOMPACTION OF DNA

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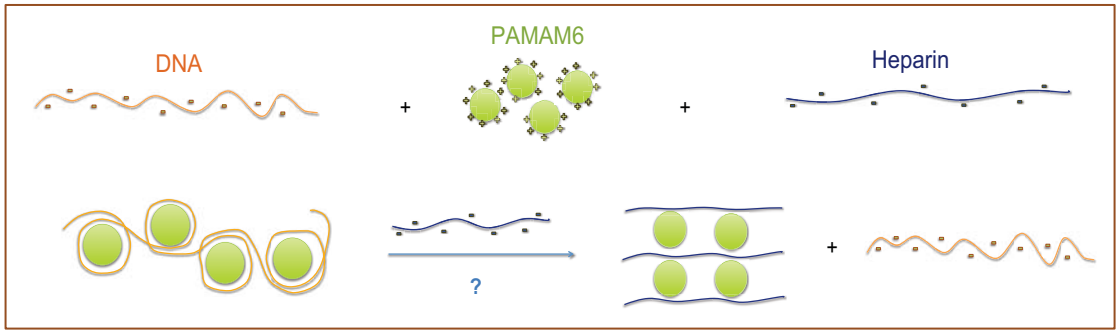
DNA compaction is the collapse of long DNA chains into well-organized condensates of complex, hierarchically organized nanostructures induced by the presence of cationic agents. Although much progress has been made in understanding underlying interaction mechanisms of *in vivo* DNA compaction, the interplay of various compaction agents and their types of interactions with DNA still raise a wealth of unanswered, fundamental questions. In particular, the hierarchical organization of chromatin is widely unclear. There, the DNA is at first wrapped around histone cores and the formed beads-on-a-string structure is successively shifted towards higher order forms of chromatin structures. The latter process involves linker histones as major antagonists.

Here, results are presented that are derived from bio-mimetic investigations of a straightforward DNA compaction model system containing only dendrimers (PAMAM 6), which can be viewed as uniformly charged cationic nanospheres, and unspecific, polydisperse DNA. Further, heparin is discovered as a decompaction agent of the formed PAMAM 6/DNA complexes. Here, negatively charged heparin competes with phosphate groups of DNA to interact with positively charged amines of PAMAM 6. We employ small angle X-ray scattering (SAXS) as the principle method of analysis, which accesses the relevant molecular length scales.



Synthesis of soft materials with intrinsic concentration gradients by thermophoresis

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INTRODUCTION: In the presence of a temperature gradient, a particle population will experience a thermophoretic force, which will drive particles to regions of high or low temperature, depending on their thermophoretic behavior.

Microfluidic devices, incorporating microchannels with cross-sectional dimensions of a few tens of microns, are ideal to exploit thermophoretic effects since temperature gradients can be established and controlled with high precision (e.g. through the use of micro Joule heaters)[1]. In particular by using biocompatible precursors (e.g. sodium alginate), it is possible to create substrates and fibers (high aspect ratio, wire-like objects) ideal for the study of cellular growth, motility or even diversification.

METHODS: A solution of *sodium alginate* is made to flow in a microchannel with a transversal temperature gradient created by an embedded joule heater[2] and a cold water flow. At the flow focusing junction the solution meet the buffer (10% dextran in water), and then the gelant solution (0.1M CaCl2 in 10% dextran aqueous solution). The buffer is used to slow down the gelation process while matching the viscosity of the sample. At the end of the microfluidic chip the formed hydrogel is extruded and collected.

The effective size of the extruded soft material is determined by the size of the microchannel and the flow rates used. In our preliminary experiments we were able to extrude strip of hydrogel of approximately 60 µm of thickness and from 100 to 400 µm width.

RESULTS: We present a new method that exploit thermophoretic transport to create material with intrinsic concentration gradients. The formed concentration gradient is then "frozen" via polymerization to create a solid (but soft) substrate that presents a gradient of mechanical properties (e.g. elasticity). Region with different concentration of sodium alginate precursor show different elastic behavior. Therefore a gradient of sodium alginate translate into rigidity modulation.

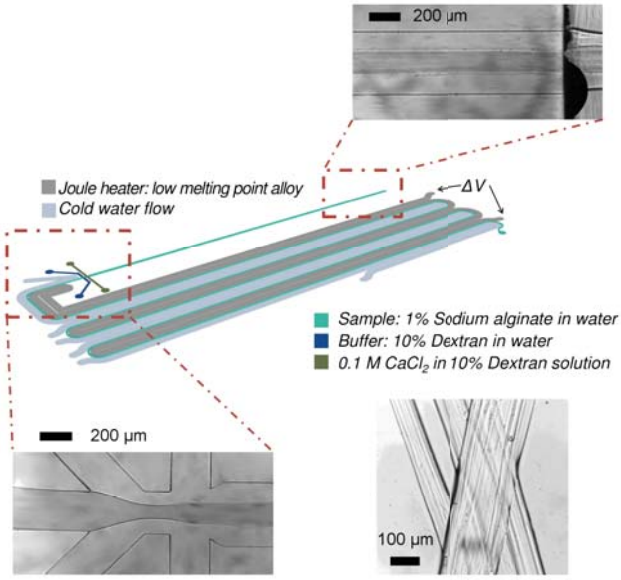

Fig. 1: microfluidic fabrication of calcium alginate soft material with intrinsic concentration gradient. Bottom right: optical image of a sample collected.

DISCUSSION & CONCLUSIONS: Our preliminary results show the feasibility to create a concentration gradient inside the hydrogel. AFM measurements are ongoing at the moment to confirm and quantify the presence of gradient of mechanical properties.

Inducing a concentration gradient by thermophoresis is possible on any polymerizable material. This will allow us to develop different kind of substrate depending on the desired application.

Future developments include the growth of cells on such a substrate to induce different motility or adhesion behavior depending on the stiffness. Variation in magnitude and on the geometry of the gradient will also be explored.

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Water Flow in Highly Confined Graphene Oxide Channels

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INTRODUCTION: Today patients suffering from chronic kidney disease are regularly treated with hemodialysis. A continuous dialysis would resemble closest the working principle of a kidney. However such artificial kidneys are today not possible, since dialysis requires a large amount of water [1]. Therefore a small and energy efficient water purification is a key technology to make artificial kidneys possible. One of the candidates for efficient water purification is a novel graphene oxide membrane. It proved to be helium tight but selectively pass water vapor [2]. The stacked graphene oxide platelets offer highly confined channels which allow water molecules to slip through. This raised the idea of using for novel water purification filters. The performance of such membranes to reject ions and other impurities is the subject of current research [3-4]. In order better evaluate graphene oxide membranes as filters; we study the behavior of water in such confined structures, through molecular dynamics simulations.

METHODS: At first we simulated water molecules and determined how well the model (TIP3P and SPC/E) agrees with characteristic properties of water. Subsequently we simulated water molecules (TIP3P water model) confined in a 3.9 nm wide channel and exposed to a constant force. In a further development graphene oxide is modeled by decorating graphene with hydroxyl and epoxy functional groups. Multiple graphene oxide layers are arranged to periodic stacks. Saline water is driven by pressure through these stacks to examine the ion rejection properties of graphene oxide.

RESULTS: The determined model characteristics such as the radial distribution function and diffusion coefficient agreed well with the properties of water [5]. Water flowing in small structures shows that, the non-slip boundary condition does not hold and there is slip between the walls and the water [6]. This results in an elevation of the parabolic velocity profile, such that the edges of the profile are clearly greater than zero. The density profile along the channel width shows a clearly increased density of water molecules in the first layer next to the walls. Molecular dynamic simulations suggest that stacked graphene oxide show an ion selectivity depending on the inter layer distance. Small inter layer distances (0.8 nm) only allow Na^+ ions to pass, since the surface is covered with negatively charged functional groups (Fig. 1). Larger inter layer distances (1.0 nm) allow both ions to pass (Fig. 2). However the simulation also suggests that this effect only applies for low water flow. At high flow rates also Cl^- ions can be dragged through the channels.

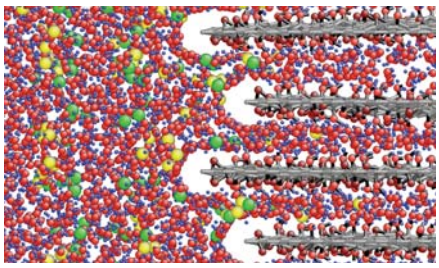

Fig. 1: Small gaps between grapheme oxide layers (0.8 nm) let water and Na^+ ions (yellow) pass, while Cl^- ions (green) are rejected.

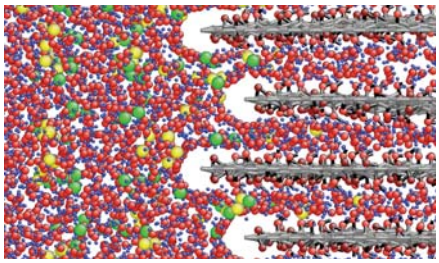

Fig. 2: Graphene oxide with large spacing (1 nm) does not show any ion selectivity.

DISCUSSION & CONCLUSIONS: The non-slip boundary condition does not hold in nanometer sized structures and slip is becoming relevant [6-7]. Despite the small structures the velocity profile is still parabolic. In the first water layer next to the walls, water molecules appear to be denser and more organized. Graphene oxide shows size dependent ion selectivity, if water density and pressure is low enough. Due to the negative charge of the functional groups, Na^+ ions can pass in-between graphene oxide layers, while Cl^- ions are rejected.

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