



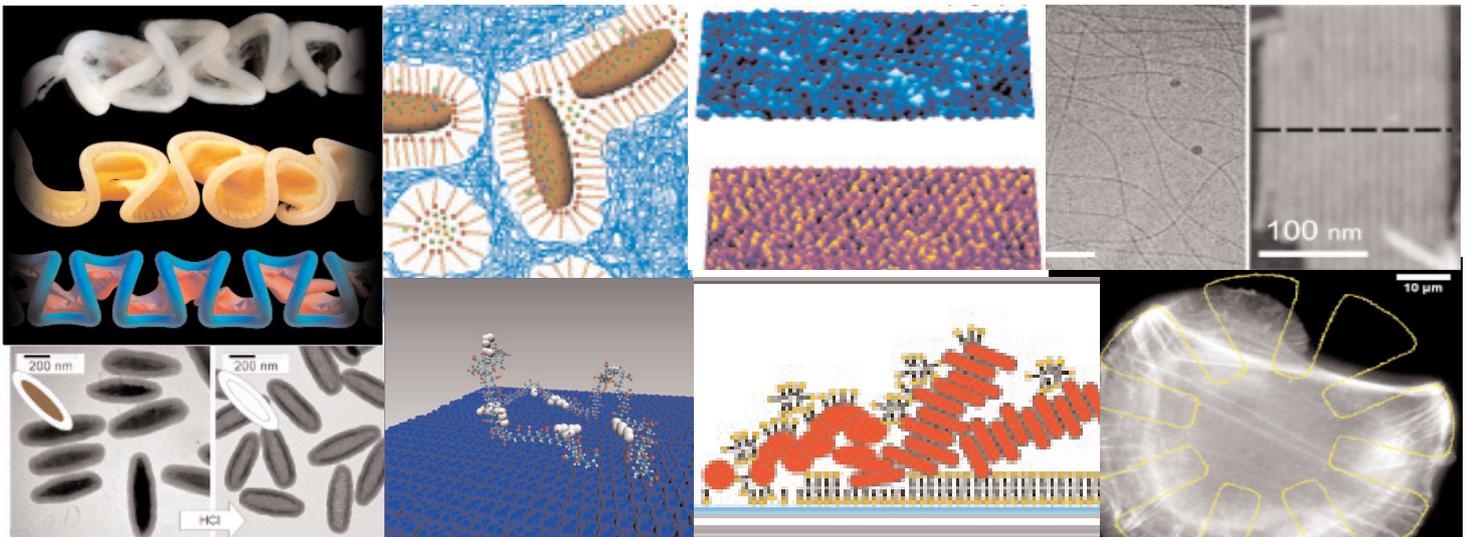
Swiss Soft Days 6

& Annual Meeting of the Swiss Group of Rheology

October 28, 2011

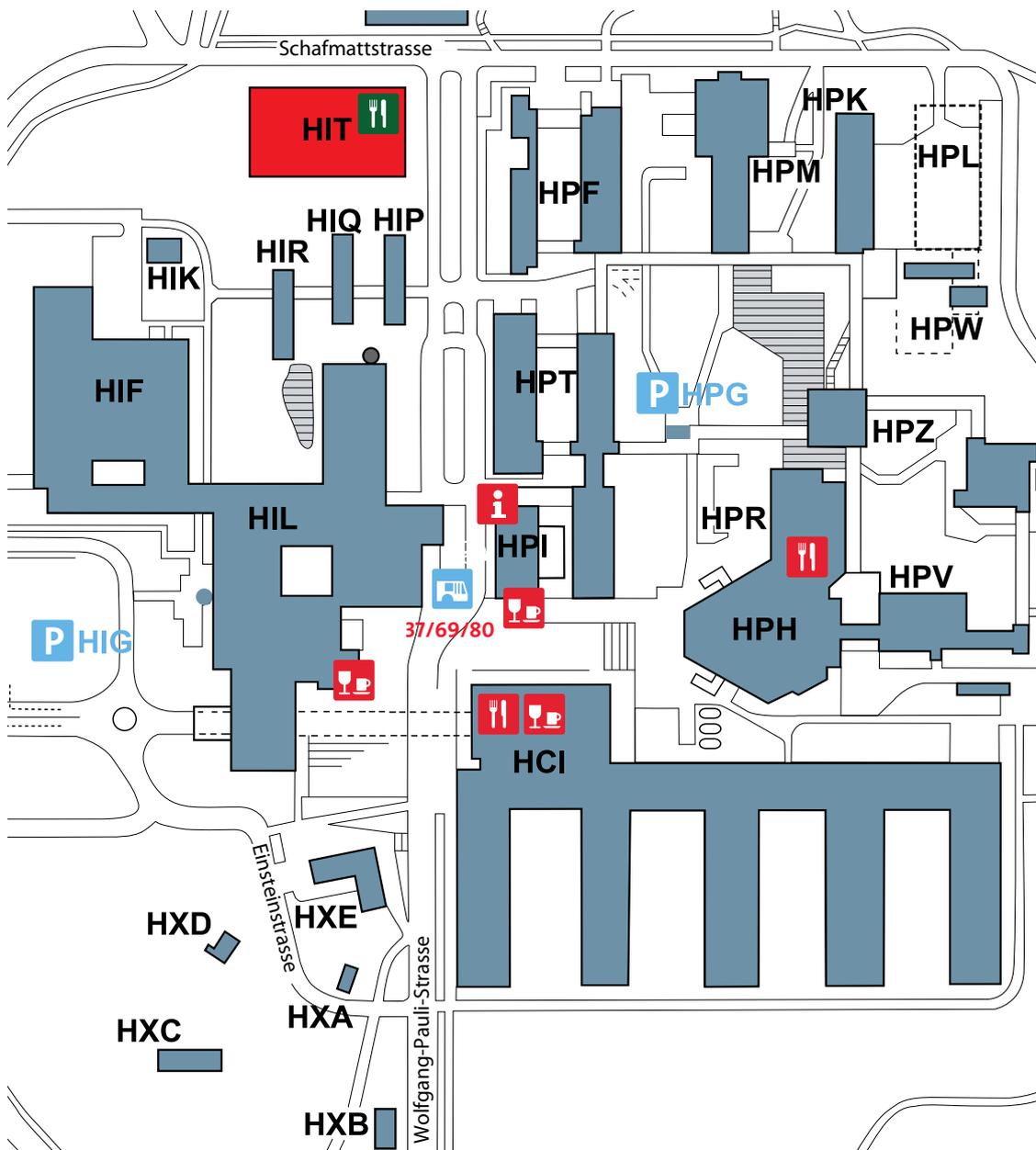
10:00 - 17:30

ETH Zurich, Building HIT E51
8093 Zurich (Hönggerberg)



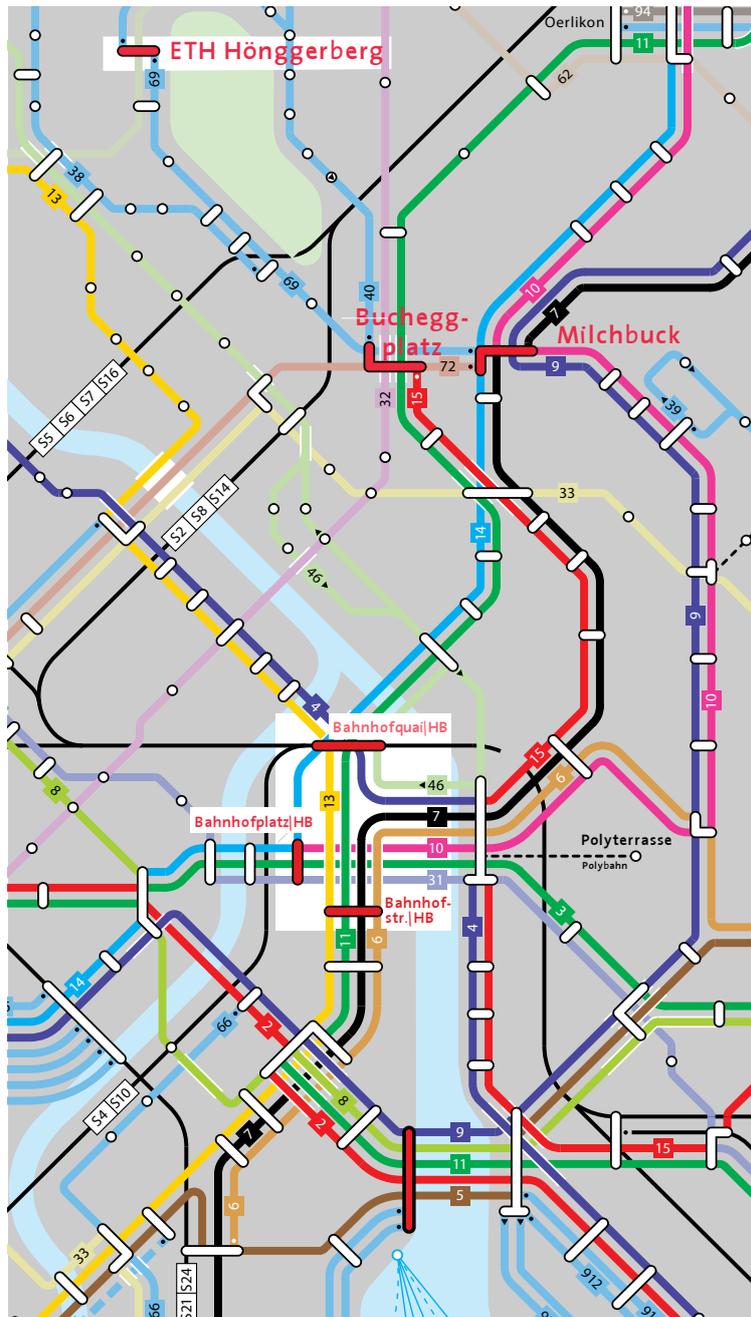
Venue at Höggerberg

ETH Zurich
Building HIT E51
8093 Zurich (Höggerberg)



Arrival information - How to get to Hönggerberg?

- 1) **Tram 11** from stop Bahnhofquai until Bucheggplatz (direction Auzelg) and from there **Bus 69** (direction ETH Hönggerberg)
- 2) **Tram 14 or 10** from stop Hauptbahnhof (direction Seebach and Flughafen, respectively) to Milchbuck and from there **Bus 69** (direction ETH Hönggerberg). Tram 7 from stop Bahnhofstrasse/HB also runs to Milchbuck.



Scientific Program

10:00 - 10:25 Registration and Coffee

10:25 - 10:30 Welcome

Session 1: Rheology

10:30 - 11:10 ***Combined methods for molecular characterization: SEC-NMR, SEC-IR to Rheo-SAXS, Rheo-NMR and Rheo-dielectric to bridge length and time scales***

Manfred Wilhelm

KIT, Karlsruhe, Germany

11:10 - 11:30 ***Rheological properties of wheat dough and corresponding model systems***

B.Schiedt¹, A.Baumann², B.Conde-Petit², T.Vilgis¹

¹ MPI Polymer Research, Mainz, Germany & ² Bühler AG, Uzwil, Switzerland

11:30 - 11:50 ***"Optical rheology" of soft core/shell particles***

D. J. Ross, R. Sigel

Adolphe Merkle Institute - University of Fribourg

11:20 - 12:30 ***Structure-function relation of comb-copolymer dispersants***

Robert Flatt

ETH Zurich

12:30 - 14:00 Lunch and Poster Session (Food 'n' Fun)

Session 2: Interfaces and biological systems

14:00 - 14:40 ***Elastic properties of colloidal glasses***

Peter Keim

University of Konstanz

14:40 - 15:00 ***Atomic force microscopy at the solid-liquid interface***

Kislon Voitchovsky, Francesco Stellacci

EPF Lausanne

15:00 - 15:20 ***The mechanism of gut loops morphogenesis***

T. Savin¹, N.A. Kurpios², A.E. Shyer³, P. Florescu³, H. Liang⁴,

L. Mahadevan³, C.J. Tabin³

¹ETH Zürich, ² Cornell University, Ithaca, USA, ³ Harvard University, Boston, USA,

⁴ USTC, Hefei, China

15:20 - 15:40 **Dynamics of stress fibers in spreading fibroblasts**
C. Labouesse, B. Vianay, J.-J. Meister
Laboratory of Cell Biophysics, EPF Lausanne

15:40 - 16:10 Coffee

Session 3: Capturing the dynamics

16:10 - 16:30 **Dynamics and structure of simple complex matters**
Martin Kröger
Polymer Physics, ETH Zurich

16:30 - 16:50 **Hydrodynamics and the fluctuation theorem**
M. Belushkin¹, R. Livi^{2,3}, G. Foffi¹
*¹ EPF Lausanne, ² Université de Cergy-Pontoise, Cergy-Pontoise, France,
³ Università di Firenze, Sesto Fiorentino, Italy*

Session 4: Lipid based systems

16:50 - 17:10 **Synthesis and applications of artificial phospholipids**
**I.A. Fedotenko¹, M.N. Holme^{1,3}, P.-Z. Zaffalon¹, B. Müller², T. Saxer³,
A. Zumbühl¹**
¹ University of Geneva, ² University of Basel, ³ University Hospitals of Geneva

17:10 - 17:30 **Phospholipid nano-discs studied in high magnetic fields**
**M. Liebi¹, J. Kohlbrecher², T. Ishikawa¹, P. Fischer¹, P. Walde¹,
E.J. Windhab¹**
¹ ETH Zurich, ² Paul Scherrer Institute

17:30 Closing remarks

COMBINED METHODS FOR MOLECULAR CHARACTERIZATION: SEC-NMR, SEC-IR AND RHEO-SAXS, RHEO-NMR AND RHEO-DIELECTRIC TO BRIDGE LENGTH AND TIME SCALES

T. Meins¹, K. Hyun¹, K. Ratzsch¹, B. Struth², T. Beskers¹, M. Cudaj¹, G. Guthausen¹,
T. Hofe³, M. Wilhelm¹

¹ Institute for Chemical Technology and Polymer Chemistry, Karlsruher Institut für Technologie (KIT), Germany, ² DESY, Hamburg, Germany, ³ PSS, Mainz, Germany

INTRODUCTION: Soft matter is frequently complex due to the interplay of molecular weight distribution, topology and chemical composition. Furthermore mechanical processing due to its underlying non-linear rheology adds further complication. In this presentation new and advanced combined methods for the unique characterisation of soft materials will be given. A focus will be towards polymeric materials and emulsions.

METHODS: The methods will be presented are centred around two topics: First the unique correlation of molecular weight distribution and chemical composition will be established via simple low field NMR spectroscopy and size exclusion chromatography (SEC). A second possibility is the correlation of the chromatographic dimension with a chemical dimension via IR-spectroscopy. In both cases substantial solvent suppression (e.g. factor 10.000) are needed. If on-line measurements are desired only about 30 seconds of measurement time are allowed.

In case of the application of non-linear mechanical forces, effects on the molecular structure and ordering at different length and time scales are expected. To evaluate these correlations three methods where either newly developed or substantially improved:

1. Rheo-NMR for small length scales and motions around the Larmor frequency
2. Rheo-Dielectric, for larger length scales at variable frequencies (0.001 Hz to 10⁶ Hz).
3. Rheo-SAXS, to investigate and quantify the kinetics and development of shear induced orientation, see Fig. 1.

RESULTS: All set ups will be explained in detail including one example of atypical measurement.

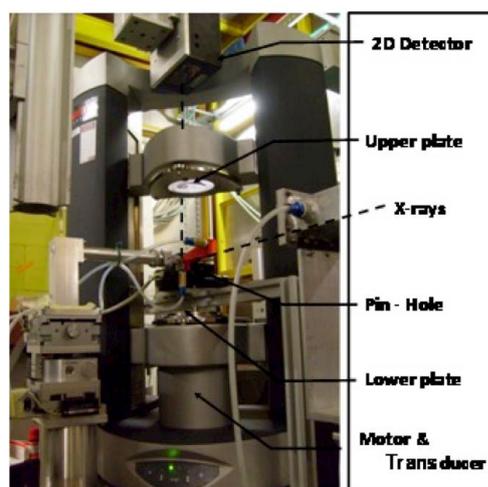


Fig. 1: Rheo-SAXS apparatus. The setup which is located at the beamline BW1 at HasyLab

REFERENCES:

<http://www.polymer.uni-karlsruhe.de/english/265.php>

ACKNOWLEDGEMENTS: We acknowledge the current and former group members and cooperation partners, thanks!

Rheological properties of wheat dough and corresponding model systems

[B.Schiedt](#)¹, [A.Baumann](#)², [B.Conde-Petit](#)², [T.Vilgis](#)¹

¹ Max-Planck Institute for Polymer Research, Mainz, Germany

² Bühler AG, Uzwil, Switzerland

INTRODUCTION: The uniqueness of wheat with regard to baking performance lies in its ability to form a viscoelastic dough upon mixing with water. The properties of wheat dough are governed by the two main polymeric constituents, protein and starch. Dough elasticity is highly related to the wheat storage proteins, which develop under hydration and energy input (kneading) into a macropolymer network, also named gluten. The starch granules are embedded into this mesh-like structure so that dough can be described as a filled polymer system. The behaviour of dough is very complex and the relationship between structure and rheological properties is still not fully understood. We present rheological tests at different deformation levels in order to provide deeper insight about starch/starch, starch/protein, and protein/protein interactions in wheat dough.

METHODS: Wheat dough were prepared by adding deionized water to either a standard wheat flour (flour 550, Swissmill, Switzerland) or model flours composed of wheat starch and gluten (Sigma, Germany). The water content of standard wheat dough was 40% wb, while for starch/gluten mixtures the water quantity was adjusted based on the respective starch and gluten fractions. For dough preparation we used a micromixer (National manufacturing, USA), in which the dough development state could be evaluated as a function of mixing time by measuring power consumption. The plate-plate geometry used for rheological dough analysis had a diameter of 25 mm diameter and was covered with sandpaper in order to avoid wall slip. For all experiments the gap width was 2 mm. Amplitude sweeps were carried out over a wide deformation range with a frequency of 1 Hz. In addition, we performed rotational measurements with a constant shear rate of 0.05 s^{-1} in order to obtain results, which are similar to the ones of classical extensional tests.

RESULTS & DISCUSSION: In Fig. 1 amplitude sweeps of dough with different gluten/starch ratios are shown. The removal of starch led to the identification of three phenomenon: (i) reduction of storage modulus G' at low deformations due to less starch/starch interactions, (ii) extension of linear viscoelastic range since a less heavily filled gluten network is harder to break, and (iii) a faster decrease of G' at large deformations, which means

that protein/protein interactions are more stress-resistant than starch/protein and starch/starch interactions.

The analysis of G' as a function of dough mixing time revealed two different mixing stages. In the hydration stage at low mixing times, G' decreased very strongly, which is presumably caused by the increase in mesh size of the gluten network as well as the dispersion of starch granules and their aggregates. In the second stage, G' still decreases but with a much lower rate, which can be explained with a slow depolymerization of gluten resulting in a less crosslinked protein network.

Rotational rheometric tests showed a qualitative difference between starch-dominated and protein-dominated systems since only the latter exhibit a strain hardening behaviour. In addition it was found that a higher shear stress is required to break optimally developed dough than undermixed or overmixed dough.

CONCLUSIONS: The main rheological properties of wheat dough can be explained by using a simplified model based on starch, proteins, and their interactions. The model was successfully applied to describe phenomena observed during dough development.

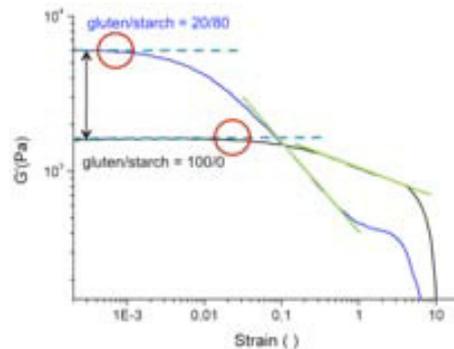


Fig. 1: Amplitude sweep of dough with different gluten/starch ratios.

"Optical rheology" of soft core/shell particles

D. J. Ross¹, R. Sigel¹

¹ Adolph Merkle Institute, University of Fribourg, Route de l'Ancienne Papeterie CP209

1723 Marly 1, <http://www.am-institute.ch>

INTRODUCTION: Core-shell particles are an essential part of soft matter, as the composite structure allows for a wide variety of stabilization methods, physical and chemical interactions, and optical properties. As the shell material is often softer and more sensitive to external forces, changes in the shape may be caused by thermal fluctuations, external fields, interfaces, and particle-particle interactions. While the scattering properties of concentric core-shell are well known, deviations from this highly symmetric case requires further investigation.

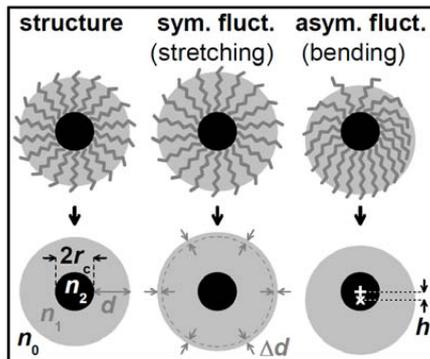


Fig. 1: Model of hairy colloid to core/shell concentric spheres. Fluctuations include fully symmetric (expansion/contraction) and asymmetric (nonconcentric)

Figure 1 shows the idealizations used to predict scattering properties. A hairy core/shell colloid is modeled as concentric spheres. Fluctuations can cause changes in the shell thickness or distortions to the soft shell, which are modeled by increases in shell thickness (d) or by nonconcentric spheres, with a distance of h between centres.

METHODS: A method is described to predict contrast factors for use in scattering experiments to allow measurements of changes in size and shape of core-shell particles, providing a method of "optical rheology". This will give quantitative measures of shell softness, as well as the reactivity to the local environment. The cases of both concentric and nonconcentric changes in structure are examined.

Changes in size and structure can be both random and controlled. Thermal fluctuations, for example,

can be used as a measure of shell softness, rather than a source of noise in measurement. Driven fluctuations are possible through the use of a charged polymer shell and an externally applied oscillating electric field.

Detection of changes in structure is accomplished through ellipsometric light scattering (ELS). ELS is analogous to the usual sense of ellipsometry, and demonstrated to be sensitive to changes in size and shape. By measuring the ratio between the horizontal (S_2) and vertical (S_1) components of the scattering, the magnitude and phase can be found:

$$S_2/S_1 = \rho = \tan(\Psi) \exp(i\Delta)$$

Modelling is done using a generalization of Mie theory to include scattering by multiple particles

RESULTS: Derivatives of the ellipsometric scattering variables $\tan(\Psi)$ and Δ are calculated using exact methods for both concentric and nonconcentric fluctuations.

Variations in derivatives are noted as a function of core and shell size, and nature and direction of fluctuation. In particular, the derivatives vary depending on the direction of nonconcentricity.

DISCUSSION & CONCLUSIONS: The calculation of derivatives of scattering variables as a function of change in size and shape allow for a measure of contrast in scattering measurements. Experimental measurements of the contrast, and therefore, the ability of the particle to deform are undergoing.

REFERENCES: ¹ A. Erbe, K. Tauer, R. Sigel; 2007; *Phys. Rev. E*; 73:031406.

² K. A. Fuller, D. W. Mackowski; 2000; in *Light Scattering by Nonspherical Particles* M.I. Mischenko et al. Eds. Academic Press.

ACKNOWLEDGEMENTS: Financial support of the Swiss National Science Foundation, NSF Project number 200021_126849/1 is gratefully acknowledged. The support of the Adolphe Merkle Institute is also acknowledged..

Structure-function relation of comb-copolymer dispersants

Robert J. Flatt

ETH Zurich; 8093 Zürich; Switzerland

Polycarboxylate comb-copolymers dispersants are key components in modern concrete, whether to reach self compaction, high strengths or high levels of Portland cement replacement. Key questions regarding their performance and robustness thereof require to define the conformation of these polymers at interfaces.

In this talk results of an extensive study by AFM in colloidal mode will be presented. It will in particular be shown that results can be very well accounted for by a scaling law that includes all main structural parameters of these polymers.

Moreover, an example is given where this data can be used at a larger scale to account for compressive yield stresses measured by centrifugal consolidation. Another example will also be given whereby these results contribute to accounting for the sensitivity that these polymers show to variation in the sulphate concentration in cement

Elastic properties of colloidal glasses

Peter Keim

Fachbereich Physik, Uni Konstanz, Germany
<http://www.keim.physik.uni-konstanz.de>

In this contribution, we present experimental results on the elastic properties of a two-dimensional colloidal glass former. Given that glasses are solids, one expects a mechanical behaviour similar to that of crystals, i.e., glasses exhibit a finite shear modulus μ . Using positional data from video microscopy, we study the displacement field and connect it to the dynamical matrix $D(q)$ via the equipartition theorem. The resulting dispersion relation of the system hints at structural change upon decreasing the temperature in the glassy state. Next, this data is used to derive the Lamé coefficients and the corresponding moduli from thermally excited modes in using continuum elasticity theory. We consider finite size and time effects and find the expected frequency dependence of the shear modulus μ . By cooling the system, the significant increase of μ allows us determine the transition temperature T_{crit} precisely. Using principal component analysis, we compute the short wavelength excitations in our system and analyse the density of states as well as the structure of normal modes in a two-dimensional colloidal system.

Atomic force microscopy at the solid-liquid interface

[Kislon Voitchovsky](#)¹, [Francesco Stellacci](#)[†]

¹ EPF Lausanne, Lausanne, Switzerland.

INTRODUCTION: Solid-liquid interfaces are ubiquitous and of fundamental importance in countless phenomena: surface electrochemistry, heterogeneous catalysis, wetting, heat transfer, folding and function of biomolecules, and self-assembly all depend on the structural organization adopted by the liquid molecules close to the surface of the solid. This so-called interfacial liquid does not behave like bulk; it tends to be more ordered and its organisation strongly depends on the local nature of the solid. Diffraction techniques can provide a very precise picture of the interfacial liquid. However, they generally require averaging over large areas, making it particularly challenging to investigate interfaces where the solid surface is inhomogeneous, for example if it presents nanoscale domains with different structural and chemical properties. Consequently, there is a strong need for methods able to image and quantify complex solid-liquid interfaces with sufficient lateral resolution.

METHODS: We use amplitude modulated atomic force microscopy (AM-AFM) to investigate the interfaces between various solids and liquids. We used solids with increasing complexity from single crystals to mixed self-assembled monolayers. We selected three liquids for their ease of use and their ability to form well structured interfaces with the solids: water, dimethylsulfoxide and an ionic liquid 1-Ethyl-3-methylimidazdium Bis(trifluoromethane sulfonyl) imide. The AFM was operated at amplitudes comparable to the size of the interface considered (~0.5-1.5nm).

RESULTS: Operated in an appropriate regime, we could derive molecular-level images of the solid-interface while simultaneously quantifying the solid-liquid interaction energy (work of adhesion). This is illustrated in Fig. 1 for a mica sample in water. The resolution crucially depends on the choice of solid-liquid combination. In the case of ionic liquids, discrete molecular layers of anions/cations could be imaged at the interface.

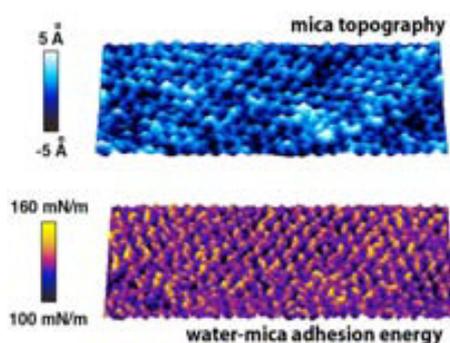


Fig. 1: AFM image of a mica surface in water. The topographic image (up) shows atomic-level resolution. Information about the local water-mica adhesion energy can also be derived, effectively quantifying the ‘wetting’ properties at the nanoscale. The xy scale is 5nm x 15nm.

DISCUSSION & CONCLUSIONS: Our results show that semi-quantitative information about the solid-liquid interface can be derived locally and with sub-nanometre resolution using AM-AFM. The approach relies on the fact that most of the tip vibration occurs within the interfacial liquid, where the vibration damping can be related to the solid-liquid work of adhesion. Furthermore the interfacial liquid can be effectively exploited to enhance the resolution with the AFM.

REFERENCES: ¹ K. Voitchovsky et al.; 2010; *Nature Nanotech.*;5:401-405.

ACKNOWLEDGEMENTS: This work has been supported by the Swiss national science foundation.

The Mechanism of Gut Loops Morphogenesis

T. Savin¹, N.A. Kurpios², A.E. Shyer³, P. Florescu³, H. Liang⁴, L. Mahadevan³, C.J. Tabin³

¹ ETH Zürich, Zürich, Switzerland. ² Cornell University, Ithaca, USA.

³ Harvard University, Boston, USA. ⁴ USTC, Hefei, China.

INTRODUCTION: Understanding the origin of the shape of organs and organism is the central goal of developmental biology. The developing vertebrate gut tube forms a reproducible looped pattern as it grows into the body cavity. This structure inherits from remodeling an initially straight tube running down the midline of the embryo. In a recent paper¹, we explained what drives the gut looping morphogenesis by elucidating the mechanism responsible for this remodeling.

METHODS & RESULTS: We first challenged several hypotheses for the loop formation using the chicken embryo as an animal model. One might think that the gut tube coils because it is restricted by the size of the abdominal cavity. But we observed that the loops remain intact and identical to their in ovo structure when the intestine is dissected from the embryo. Another possible mechanism is a differential cell proliferation that forces the tissue to curve at specific locations. We measured however that the number of mitotic cells was not different at the bend points, thus making this hypothesis also unlikely.

The intestine is composed of the gut tube and of the dorsal mesentery, a thin membrane suspending the tube to the body, and that guides the vascularization of the organ. The tube is attached to the periphery of the mesentery over its whole length. When both were surgically separated, we observed that the gut spontaneously uncoiled into a straight tube, while the mesentery contracted like a relaxed rubber band. Separate measurements on each component showed that the tube grows about 3 times faster than the mesentery, and this differential growth indeed puts the mesentery under tension, producing the elastic forces that forms and hold the loop in place.

A simple physical mimic, using a differentially strained composite of a flexible rubber tube and a soft latex sheet is consistent with this mechanism and produces similar patterns, as seen in Fig. 1. To quantify the in-vivo and in-vitro observations, we implemented numerical simulations that reproduce the looping pattern, based solely on the geometry, elasticity and relative growth of the tissues as input parameters. We developed new rheological tools to measure the Young's modulus of the embryonic

tissues. We used histology to measure their thickness. We show in Fig. 1 a simulated configuration, obtained with the biophysical measurements as input. The result compares well with the observed pattern in the biological gut and its physical simulacrum. We then derived a mathematical theory for the number, size and shape of intestinal loops. The predictions of our theory are quantitatively consistent with observations of intestinal loops at different stages of development in the chick embryo. From a comparative perspective, our model is similarly robust in accounting for the qualitative and quantitative variation in the distinct gut looping patterns seen in a variety of species including the quail, finch and mouse, for which we repeated the morphometric and mechanical measurements.



Fig. 1: The top image is a millimetre size gut dissected from of a chicken embryo; in the middle, the centimetre size physical mimic is made of rubber tube and membrane; at the bottom, we show a rendering of our simulations.

CONCLUSION: The approach we used here to modeling the formation of organs contrasts with the recent molecular/genetic emphases in developmental biology, which alone cannot explain large-scale morphologies.

REFERENCES: ¹ T. Savin, N.A. Kurpios, A.E. Shyer, P. Florescu, H. Liang, L. Mahadevan & C.J. Tabin; 2011; Nature; 476:57-62.

Dynamics of Stress Fibers in Spreading Fibroblasts

C. Labouesse¹, B. Vianay¹, J.-J. Meister¹

¹ Laboratory of Cell Biophysics, EPF Lausanne, Lausanne, Switzerland

INTRODUCTION

Actin networks are involved in nearly every single cellular processes. Each cell function is supported by a specific architecture and selected interactions with other proteins, polymers or the extra-cellular matrix (ECM). Most interesting are the intercalated bundles of actin and myosin (stress fibers), which are responsible for cell contractility. When connected to the ECM at cell-matrix adhesion complexes, they are also involved in the mechanosensing machinery. The initiation of these structures at the front of the lamellum is therefore critical for various cell processes requiring motion, contraction, or signal transduction with the microenvironment. Though the properties of lamellipodial actin at the leading edge have been extensively studied, it is not fully known how the lamellipodium/lamellum border is formed, and what happens at this interface. We track the formation, stabilization and dynamics of both stress fibers and focal adhesions using timelapse imaging of fibroblasts expressing actin and vinculin tagged with a fluorophore. Cells are seeded on specific adhesive micropatterns with which we control the localization of adhesion sites and therefore the spreading geometry by alternating adhesive branches and non-adhesive gaps a few μm wide.

METHODS

Substrate fabrication : Micropatterned substrates are fabricated with UV-photolithography at the Center of MicroNanootechnology (CMI). Glass coverslips are first treated with silane (ODTS). They are then coated with positive photoresist, and insolated through a mask by UV light. After development of the insolated resist, some adhesive protein (typically fibronectin) is adsorbed on the patterned surface.

Cell Transfection : 48 hours prior to seeding the cells on the patterns, fibroblasts are transiently transfected with LifeActin-EGFP. Transfection are stable over several days, and during live imaging up to 10 hours.

RESULTS

We observe that above a given distance between adhesions, an actin bridge parallel to the leading edge and rich in myosin II is formed and reinforced. As the leading edge advances, nascent adhesions mature under the tension exerted by

actin filaments. The latter stabilize into dorsal stress fibers, along which transverse arcs slide centripetally, eventually being either disassembled or fusing with dorsals to create a ventral stress fiber (connected to focal adhesions at both ends). After the initial spreading phase, we observe cytoskeletal remodeling. Ventral stress fibers are further aligned along one preferential axis to redistribute tension within the cytoskeleton and on adhesion sites.

These experimental results and quantification of stress fibers velocities will be used to build a simplified model of cell spreading, based on mechanical properties of stress fibers and focal adhesions. The simulations output will shed light on how these structures interact dynamically.

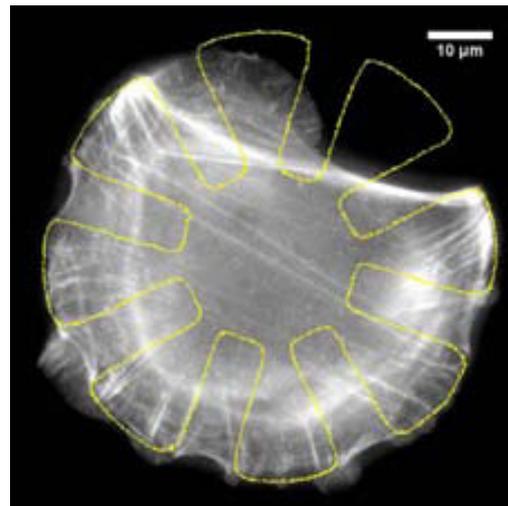


Fig. 1: A subcutaneous fibroblast spread on the pattern (yellow overlay), and transfected with LifeActin EGFP.

ACKNOWLEDGEMENTS

I wish to thank our lab assistants, Josiane Smith-Clerc and Carine Ben Adiba for their help.

Dynamics and structure of simple complex matters

Martin Kröger

Polymer Physics, Institute of Polymers, Department of Materials,
ETH Zurich, Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland
<http://www.complexfluids.ethz.ch>

On one hand this short talk is concerned with recent, both coarse-grained and generic, models for the dynamics and structure of thick (dendronized) polymers [1, 2], networks and gels [3], and self-strengthening materials [4]. On the other we exemplify on how to obtain a molecularly derived constitutive equation for low-molecular polymer melts from thermodynamically guided simulation [5]. And we quantify chain reptation in entangled polymer melts under flow [6]: from atomistic onto the tube model [7].

References

- [1] Y. Ding and M. K., Phase behavior and formation dynamics of helically wound networks: generalized Janus chain model, *Macromolecules* 2009, 42, 576.
- [2] W. Zhuang, E. Kasemi, Y. Ding, M. K., A.D. Schlüter and J.P. Rabe, Self-folding of charged single dendronized polymers, *Adv. Mater.* 2008, 20, 3204.
- [3] M. K., O. Peleg, Y. Ding and Y. Rabin, Formation of double helical and filamentous structures in models of physical and chemical gels, *Soft Matter* 2008, 4, 18.
- [4] I.G. Salib, G.V. Kolmakov, B.J. Bucior, O. Peleg, M. K., V. Vogel, K. Matyjaszewski and A.C. Balazs, Using mesoscopic models to design strong and tough biomimetic polymer networks, *Langmuir* 2011, in press.
- [5] P. Ilg and M. K., Molecularly derived constitutive equation for low-molecular polymer melts from thermodynamically guided simulation, *J. Rheol.* 2011, 55, 69.
- [6] J.M. Kim, D.J. Keffer, M. K. and B.J. Edwards, Rheological and entanglement characteristics of linear chain polyethylene liquids in planar Couette and planar elongational flows, *J. Non-Newtonian Fluid Mech.* 2008, 152, 168.
- [7] P.S. Stephanou, C. Baig, G. Tsolou, V.G. Mavrantzas and M. K., Quantifying chain reptation in entangled polymer melts: Topological and dynamical mapping of atomistic simulation results onto the tube model, *J. Chem. Phys.* 2010, 132, 124904.

Hydrodynamics and the Fluctuation Theorem

[M. Belushkin](#)¹, [R. Livi](#)^{2,3}, [G. Foffi](#)¹

¹ EPF Lausanne, Lausanne, Switzerland.

² Université de Cergy-Pontoise, Cergy-Pontoise, France.

³ Università di Firenze, Sesto Fiorentino, Italy.

INTRODUCTION: It is well-known that the Laws of Thermodynamics hold “on average”, i.e. are expressed in terms of ensemble-averaged quantities. At length- and time-scales where the effects of fluctuations – in particular, of thermal fluctuations, are pronounced, the Laws no longer need to be exactly satisfied.

The fluctuation theorem is a fundamental result in physics. It quantifies the probability of observing violations of the Second Law of Thermodynamics in small systems at short times⁴, i.e. quantifies the probability of observing phase-space trajectories which lead to entropy consumption and not production. While its relevance on the mesoscopic level is well-known, its validity in the presence of long-range, long-time corrections – such as hydrodynamic correlations, has been unclear⁵.

METHODS: We perform computer simulations employing the method of multiparticle collision dynamics (MPC) which is known to correctly describe thermal fluctuations and hydrodynamic interactions on coarse-grained length- and time-scales⁶⁻⁸ even at very short times, as we have recently demonstrated^{9,10}. Following earlier investigations⁵, we study the local entropy production in a simple fluid in planar shear flow.

RESULTS: We demonstrate¹¹ that in a system possessing long-range and long-time correlations, specifically hydrodynamic correlations, entropy production is a collective process. We find that the fluctuation theorem does hold at arbitrary observation (averaging) times, provided a specific hydrodynamic scaling of the observation volume is taken into account. Furthermore, we show that it is a simple diffusion process which is responsible for the observed scaling: the effective volume within which entropy production is being measured is greater than the physical measurement volume by a diffusive length scale which depends on the properties of the medium and the measurement time.

DISCUSSION & CONCLUSIONS: Our results bear important consequences for experiments aimed at putting the fluctuation theorem to the test. In particular, we demonstrate^d how correlations in

the system should be accounted for in the interpretation of measurement results.

REFERENCES:

- ¹ D. J. Evans et al, PRL 71, 2401 (1993)
- ² G. Gallavotti, E. Cohen, PRL 74, 2694 (1995)
- ³ J. Kurchan, J. Phys. A31, 3719 (1998)
- ⁴ D. Evans, D. Searles, Adv. Phys. 51, 1529 (2002)
- ⁵ F. Bonetto, J. L. Lebowitz, Phys. Rev. E 64, 056129 (2001)
- ⁶ J. T. Padding, A. A. Louis, Phys. Rev. E 74, 031402 (2006)
- ⁷ R. Kapral, Adv. Chem. Phys. 140, 89 (2008)
- ⁸ G. Gompper et al., Adv. Polym.Sci. 221, 1 (2009)
- ⁹ T. Franosch, M. Grimm, M. Belushkin, F. Mor, G. Foffi, L. Forró, Nature 47885 (2011)
- ¹⁰ M. Belushkin, R. G. Winkler, G. Foffi, JPC B, in print (2011) [arXiv: 1108.5271]
- ¹¹ M. Belushkin, R. Livi, G. Foffi, PRL 106, 210601 (2011)

ACKNOWLEDGEMENTS: M. B. and G. F. acknowledge financial support by the Swiss National Science Foundation (Grant No. PP0022_119006).

Synthesis and Applications of Artificial Phospholipids

I.A. Fedotenko¹, M.N. Holme¹⁻³, P.-Z. Zaffalon¹, B. Müller², T. Saxer³, A. Zumbuehl¹

¹ University of Geneva, Geneva, Switzerland. ² University of Basel, Basel, Switzerland. ³ University Hospitals of Geneva, Geneva, Switzerland.

INTRODUCTION: In our developed societies, heart attack is the number one killer. Targeted drug delivery to stenosed vessels, however, is hampered by the lack of specific bio-markers in the critically constricted arteries. As an alternative, so we hypothesized that one might take advantage of the significantly increased shear stress in the narrowed arteries.

For this purpose we have investigated the application of endogenous shear stresses in the diseased heart vasculature for targeted release of a payload from large, 100 nm unilamellar vesicles (LUVET₁₀₀) made from an artificial diamido-phospholipid. The observed results are not seen in vesicles formulated with natural phospholipids.

METHODS: The liposomes were formed from a thin film of lipids as described by Olson et al¹ Pad-PC-Pad, a symmetrical 1,3-diamido-phospholipid was synthesized according to the procedure reported by Fedotenko et al.² (fig 1.) and converted to the choline by exhaustive methylation with dimethylsulfate. The vesicles were loaded with 50 mM 5(6)-carboxyfluorescein, which acts as a fluorescent release marker. The external buffer was 10 mM HEPES at pH 7.4.

An *in vitro* model of a healthy and critically constricted coronary artery was built from PMMA and combined in a circulatory set-up with a Medtronic Bio-Pump (Bit-Medical, Switzerland). The pressure, flow rate and temperature were maintained within physiological conditions. Vesicles were passed through this model either one or 40 times and fluorescence release was detected. Shaking experiments were carried out using an IKA Vortex Genius 3. Vesicles were shaken in a vial for periods between 0 and 60 seconds and fluorescence release was measured. As a control, the stability of the vesicle formulations over 6 days was studied.

RESULTS: Formulations containing only the artificial phospholipid Pad-PC-Pad were found to release an additional 51% of their payload after the first pass through the critically constricted artery model with a shear stress of about 10 Pa, whereas in a common artery model with a shear stress of about 2 Pa, only 27% additional release was observed. In contrast, vesicles formulated from mixtures of the natural phospholipid eggPC and 0-1 mol% of the surfactant Brij S10 were found to

release a total of only an additional 14% of their payload after 40 passes through the critically stenosed artery model, and 3% after 40 passes through a common artery model. In both cases, background release was around 20%.

The shaking experiments indicated that Pad-PC-Pad behaves different from other vesicles formulated from natural phospholipids. Although all vesicle formulations are stable on the bench for up to 6 days, Pad-PC-Pad vesicles were found to release 40% of their contents after shaking for only 1 minute.

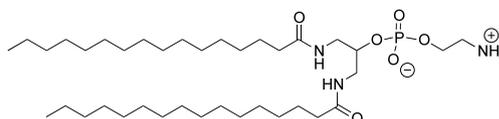


Fig. 1: Chemical structure of the artificial phospholipid Pad-PE-Pad containing a symmetrical 1,3 substitution pattern and two amides at the backbone between hydrophobic tails and the hydrophilic head group².

DISCUSSION & CONCLUSIONS: The release from pure Pad-PC-Pad vesicles in the *in vitro* model is an order of magnitude higher than formulations based on eggPC. Pad-PC-Pad is the only formulation that is stable on the bench but instable under shaking. These results demonstrate that shear stress sensitive nano-containers can be fabricated with potential applications, e.g., in targeted drug delivery to critically stenosed vessels.

REFERENCES: ¹ F. Olson, C.A. Hunt, F.C. Szoka, W.J. Vail, and D.A. Papahadjopoulos, *Biochim. Biophys. Acta*, 1979, 557, 9. ²I.A. Fedotenko, P.L Zaffalon, F. Faveager and A. Zumbuehl, *Tetrahedron Lett.* 2010, 51, 5382.

ACKNOWLEDGEMENTS: Support from the following sources is gratefully acknowledged: Swiss National Science Foundation, NRP 62 "Smart Materials", COST D43.

Phospholipid nano-discs studied in high magnetic fields

M.Liebi¹, J.Kohlbrecher², T.Ishikawa³, P.Fischer¹, P.Walde⁴, E.J.Windhab¹

¹Laboratory of Food Process Engineering, ETH Zurich, Switzerland; ²Laboratory for Neutron Scattering, PSI Villigen, Switzerland; ³Department of Biology, ETH Zurich, Switzerland, ⁴Department of Materials, ETH Zurich, Switzerland.

INTRODUCTION: Phospholipids are amphiphilic molecules and main components of biological membranes. Due to their diamagnetic susceptibility anisotropy, phospholipids have a preferred orientation in magnetic fields. For single molecules the disordering thermal fluctuation energy exceeds the magnetic orientation. However for a phospholipid bilayer with parallel aligned molecules the diamagnetic susceptibility becomes additive and an orientation in magnetic field is possible.¹ Anchoring of paramagnetic lanthanide ions to the membrane with the help of a phospholipid-chelator can further increase magnetic orientability.²

METHODS: The phospholipid nanodiscs were prepared by lipid film hydration, followed by freeze-thaw cycles and extrusion through a polycarbonate membrane. The system was studied with small angle neutron scattering (SANS) measurements in a magnetic field of 8 T, cryo-transmission electron microscopy (cryo-TEM), and birefringence measurements in magnetic fields.

RESULTS: Bicelles are disc-shaped aggregates, normally composed of bilayer-forming phospholipids in the center and more wedge-shaped molecules covering the highly curved edge region of the bicelle.

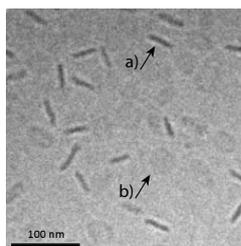


Fig. 1: Cryo-TEM micrograph of bicelles formed by a mixture of DMPC and DMPE-DTPA with complexed lanthanides in edge-on (a) and face-on view (b).

A new type of bicellar disks has been developed composed of the phospholipid DMPC and the phospholipid-chelator DMPE-DTPA with complexed lanthanides.³ In this mixture, only one type of fatty acid tail, myristoyl, is present, in contrast to conventional bicelles. We assume that partial lipid segregation occurs, due to the large

head-group of the DMPE-DTPA with the complexed lanthanides, accumulating preferably in the edge region of the bicelle as shown in the sketch (Fig. 2).

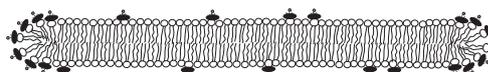


Fig. 2: Sketch of a bicelle (cross section of an edge-on view) formed by DMPC (white) and DMPE-DTPA (black).

The radius of the bicelles depends on the molar ratio of DMPC:DMPE-DTPA. As shown in Fig. 1 for a molar ratio of DMPC:DMPE-DTPA of 4:1 and a total lipid concentration of 15 mM, the resulting bicelles have a radius of 20 nm and a bilayer thickness of about 4 nm. Weak alignability in a magnetic field of 8 T is observed if the paramagnetic lanthanide Tm^{3+} is used as shown with SANS in magnetic fields.³

With the implementation of cholesterol into the membrane the magnetic orientation was strongly increased (Fig. 3).

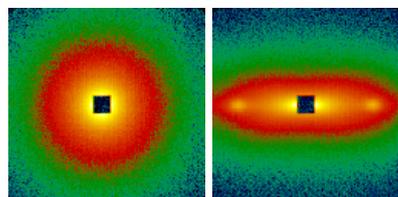


Fig. 3: SANS 2D pattern from mixtures of DMPC, cholesterol, and DMPE-DTPA with Tm^{3+} at 5°C, measured at 0T (left) and 8T (right).

We propose that cholesterol act as a spacer between the large headgroup of the chelator lipid, thus allowing more of lanthanide ions entering the bilayered center of the bicelle and therewith contributing to the magnetic orientation. With increasing cholesterol concentration, the radius of the bicelle increased, as less of the chelator-lipid is available to cover the edges.

REFERENCES: ¹K.Binnemans and C.Görller-Walrand; 2002; Chem Rev; 102:2303-45. ²R.S.Prosser, V.B.Volkov, and I.V.Shiyanovskaya; 1998; Biophys J 75:2163-69. ³P.Beck, M.Liebi, J.Kohlbrecher, et al.;2010; Langmuir 26:5382-87.

Poster Session (12:30 - 14:00)

(listed in alphabetical order of the first author)

Field- and flow-effects on the anisotropy of the magnetoviscous effect in ferrofluids

Aparna Sreekumari, Patrick Ilg

ETH Zurich

Rheological effects on the dispersion of emulsion during spray processing

Bipro N. Dubey, Erich J. Windhab

ETH Zurich

Control of Anisotropic Particle Suspensions for Bioinspired Composite

R. Erb, R. Libanori, A. Studart

ETH Zurich

Magnetically Actuated Emulsions Systems

R. Erb, J. Sander, C. Denier, A.R. Studart

ETH Zurich

Three Dimensional Flow of Colloidal Glasses

T.F.F. Farage, J.M. Brader

University of Fribourg

Rheology modifying cement admixtures

L. Ferrari ^{1,2}, J. Kaufmann ¹, F. Winnefeld ¹

¹EMPA Duebendorf, ² TU Munich Zurich

Adsorption behaviour and lubricating properties of amphiphilic polymers

Giacomo Fontani, Rowena Crockett, Roberto Gaspari, Daniele Passerone, Nicholas Spencer

ETH Zurich

Magnetically-assisted structural control of porous silica monoliths

M. Furlan, D. Parakkal, M. Lattuada

ETH Zurich

Effect of viscosity ratio, film drainage time and emulsifier type on avalanches of coalescence events in emulsion

Deniz Z. Gunes, Mathilde Bercy

Nestlé Research Center, 1000 Lausanne 26

Regularized Landau-de Gennes free energy for nematics

Patrick Ilg

ETH Zurich

From Powders to Collapsible Structures/"Living Quicksand": Discrete Modeling

D. Kadau, H. J. Herrmann

ETH Zurich

Atomic Force Microscopy as a Tool to Investigate the Properties of Polyglycerol Ester Foams

R. Keller¹, C. Curschellas², R. Berger¹, U. Rietzler¹, D. Fell¹, H.J. Limbach³, H.-J. Butt¹

¹ MPI Polymer Research, Mainz, Germany, ² ETH Zürich, ³ Nestlé Research Center, 1000 Lausanne 26

CW and Pulse EPR Spectroscopy on Polymer-Clay Nanocomposites

U. Kielmann, I. GarciaRubio, E. Barthazy, A. Bittermann, G. Jeschke

ETH Zurich

Photo-responsive reversible aggregation and dissolution of rod-like polypeptide diblock copolymers

Venkata Krishna Kotharangannagari^{1,2}, Antoni Sánchez-Ferrer², Janne Ruokolainen³, and Raffaele Mezzenga²

¹ University of Fribourg, ² ETH Zurich, ³ AALTO University, Helsinki, Finland

A new level of structural control on amyloid fibrils: self-assembled lysozyme

C. Lara, I. Usov, J. Adamcik, S. Jordens, R. Mezzenga

ETH Zurich

Liquid transport in sheared wet granular matter

R. Mani, D. Kadau, H.J. Herrmann

ETH Zurich

Dynamics and ordering of ellipsoidal nanoparticles: From low to high volume fractions

Ilya Martchenko^{1,2}, Jérôme J. Crassous^{1,2}, Chantal Rufier³, Hervé Dietsch¹, Mathias Reufer⁴, Peter Schurtenberger²

¹ University of Fribourg, ² Lund University, Lund, Sweden, ³ INSA de Lyon, Villeurbanne, France, ⁴ University of Edinburgh, Edinburgh, UK

Hydrogels for Control of Cell Morphology and Differentiation

R. Mhanna¹, J. Becher², M. Schnabelrauch², M. Zenobi-Wong¹

¹ ETH Zurich, ² INNOVENT e.V., Jena, Germany

A systematic analysis of protein covered air/water and oil/water interfaces

A. Mütze, V. Mitropoulos, E.J. Windhab, P. Fischer

ETH Zurich

How to obtain a galactomannan standard for solution rheology?

M. Pollard, S. Illmann, E.J. Windhab, P. Fischer

ETH Zurich

The mechanism of membrane interaction and disruption by α -Synuclein

N. Reynolds¹, A. Soragni², M. Rabe¹, D. Verdes¹, E. Liverani², S. Handshin², R. Riek², S. Seeger¹

¹University of Zurich, ²ETH Zurich

Dilatational Rheology of Protein Fibers at Fluid-Fluid Interfaces

P.A. Rühls, S. Danner, S. Jördens, I. Lucio, E.J. Windhab, R. Mezzeng, P. Fischer

ETH Zurich

Edible Supramolecular Chiral Nanostructures by Self-Assembly of an Amphiphilic Phytosterol Conjugate

A. Sánchez-Ferrer, J. Adamcik, R. Mezzenga

ETH Zurich

Liquid-Crystalline Elastomers in Microdevices

A. Sánchez-Ferrer^{1,3}, T. Fischl², M. Stubenrauch², A. Albrecht², H. Wurmus², M. Hoffmann², H. Finkelmann³

¹ETH Zürich, Zürich, Switzerland, ²Technische Universität Ilmenau, Ilmenau, Germany, ³Albert-Ludwigs-Universität, Freiburg, Germany

Adsorption of polydisperse soft shell nanoparticles on liquid interfaces: A numerical study

Konrad Schwenke, Emanuela Del Gado

ETH Zurich

Fluid Characterization by Vibration Sensors Oscillating in Multiple Modes

Thomas Wattering, Tobias Brack, Jürg Dual

ETH Zurich

Field- and flow-effects on the anisotropy of the magnetoviscous effect in ferrofluids

Aparna Sreekumari¹, Patrick Ilg¹

¹*Polymer Physics, ETH Zürich, Wolfgang-Pauli Str. 10, CH-8093 Zürich*

Motivation

Ferrofluids are stable colloidal suspensions of ferromagnetic nano particles. One of the most important features of ferrofluids is the relative change in viscosity with the change in magnetic field, known as Magneto Viscous Effect (MVE)[1]. Anisotropy of MVE has been proved in a classical experiment by McTague[2]. Shliomis has given a theoretical explanation that the anisotropy of MVE results only from the misalignment of vorticity and magnetic field direction[3]. Zubarev and Iskakova[4] studied the effect of rigid, chain like aggregates on the effective rheological properties of ferrofluids. They predicted that these chain like aggregates give rise to a more complicated anisotropy of the viscosity compared to Shliomis' theory. To get a complete picture of dynamics of ferrofluids, a thorough understanding of the anisotropy of MVE is required. And also, the study of anisotropy is a very sensitive test of ferrofluid theories and it is crucial for modeling ferrofluid flow in practical applications with more complicated geometries.

Plan and Simulation Details

Our aim is to get an improved understanding of the anisotropy of the Magneto Viscous Effect. We study the changes in ferrofluid dynamics, due to the presence of a flow and an applied magnetic field. The typical example of anisotropic fluid is liquid crystals, as in the liquid crystals, we do the same procedure to find

the anisotropy by doing different simulations with different orientations of the magnetic field with respect to the flow direction. We do Langevin dynamics of many interacting dipolar particles. We would like to observe magnetisation, structural properties and stresses by following their translational and rotational motion. By comparing the result with experimental work, we hope to get a clear idea about the physical mechanism of observed anisotropy of MVE. Interpretation of the result will be facilitated by the use of magnetite and cobalt based ferrofluids that have been synthesised and carefully characterised in the last years. Careful comparisons with well characterized ferrofluids allow to choose realistic model parameters, with the help of experiments done by Odenbach group[5].

References

- [1] S. Odenbach *Magnetoviscous Effects in Ferrofluids*, Lecture Notes in Physics **71**, Springer (2002).
- [2] J. P. McTague *Magnetoviscosity of Magnetic Colloids*, The Journal of Chemical Physics **51**, 1, (1969).
- [3] M. I. Shliomis, Sov. Phys. JETP **34** (1972) 1291.
- [4] A. Yu. Zubarev and L. Yu. Iskakova. Phys. Rev. E **61** (2000) 5415.
- [5] M. Gerth-Noritzsch, D. Yu Borin and S. Odenbach, J. Phy. Condens. Matter 2011, in press.

Rheological effects on the dispersion of emulsion during spray processing

Bipro N. Dubey and Erich J. Windhab

Laboratory of Food Process Engineering, IFNH, ETH Zurich, Switzerland

INTRODUCTION: Spraying of dispersed system is a growing field of interest for different industrial application. Double emulsions (DE) are widely used in many industries for encapsulation. On the other hand, DE is thermodynamically unstable. Therefore, production of solid particle from emulsion could be an alternative way of our interest through spray drying or spray-chilling. Since DE is very much sensitive by the mechanical treatment (e.g. spraying), present investigation is of interest to study the sustainability of the emulsion-microstructure during spraying^{1,2}. Therefore, the impacts of emulsions' rheology (shear/elongational viscosity, elasticity etc.) have been studied.

METHODS: Simple emulsion was prepared by rotor-stator device (Polytron PT6000, Kinematica AG). Whereas, double emulsions (O/W/O and W/O/W) were prepared by a two-steps method by using rotating membrane emulsification process. The extensional and shear viscosity, viscoelasticity, and surface tension of the continuous phase and emulsions were measured by a capillary break-up rheometer (CaBER-1, HAAKE), shear rheometer (Anton Paar, Physica 300) and tensiometer (PAT-1, SINTERFACE tech.) respectively. The drop size distribution of emulsion was investigated by laser diffraction particle size analyzer LDPSA (LS 13320, Beckman Coulter, Inc.) and by inverse light microscopy (Nikon). The microstructure of solid particles was investigated by cryo-scanning electron microscopy (cryo-SEM), and was compared with respective light microscopic pictures.

RESULTS: Present study includes the impact of mechanical treatment during spraying process on the structure of simple (SE) and double emulsions (DE). We have found that the size and size distribution of secondary droplets (emulsion droplet) are highly influenced by the rheological properties of the emulsions during spraying. The dispersion of emulsion is caused by (i) the rheology of dispersed phase & continuous phase, (ii) elongational flow inside the nozzle, (ii) the way of liquid & gas phase mixing (internal and external mixing), and (iii) impact of the gas to liquid mass ratio (GLR). The microstructure changes of simple and double emulsions were investigated for different GLR (gas liquid ratio) during spraying process at constant liquid flow rate of 0.05 L/min

or 0.2 L/min. In general, the droplet size decreases with increasing air pressure (maximum air pressure 3 bar). We have also found that the dispersion of emulsions is highly influenced by the viscosity of dispersed phase.

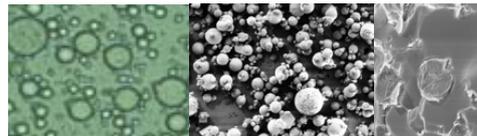


Fig. 1: (left) The microscopic image of double emulsion (W/O/W) that was used for the production of solid powder (middle) by using prilling process, where as the internal microstructure (right) of prills was investigated by cryo-scanning electron microscopy (SEM) with different spray-process conditions.

DISCUSSION & CONCLUSIONS: The emulsion flow inside the nozzle has a big influence on structure due to high stresses acting. Droplet size of emulsion decreases with increasing liquid phase (emulsion) flow rate, since the stress inside the nozzle is a function of liquid flow rate (or velocity). Impact of gas-liquid mixing-experience of twin-fluid atomizer on secondary droplet was also observed with different GLR conditions. The critical effective gas We (Weber number) has been defined for different atomizers. It was found that the secondary drop diameter decreases prominently above the critical value, which may lead to change the structure of DE to SE (phase separation). In addition, prilling experiment was carried out for producing solid particles of emulsions and detail structure was investigated by cryo-SEM (Fig. 1).

REFERENCES: ¹ Dubey, B. N., Duxenneuner, M. R., and Windhab, E. J., 2010 ILASS, Brno, Czech; Rep., Sept. 6-8.

² Dubey, B. N., Duxenneuner, M. R., Küchenmeister, C., Fischer, P., and Windhab, E. J., 2011; 24th ILASS, Estoril, Portugal, September 5-7.

ACKNOWLEDGEMENTS: The project is funded by DFG (German Research Foundation) under Priority Programme (SPP – 1423).

Control of Anisotropic Particle Suspensions for Bioinspired Composite Technology

[R.Erb](#)¹, [R.Libanori](#)¹, [A.Studart](#)¹

¹ ETH Zürich, Zürich, Switzerland.

INTRODUCTION: Due to the large strength to weight ratio of composites, their implementation as load-bearing materials is exponentially growing especially in aerospace, the automobile industry, and construction. The majority of commercial composites today are produced with continuous aligned fibers that lead to significant material strength along a single axis. To gain total in-plane strength, industrial users laminate sheets of fiber composites together in different orientations. Though this process necessarily weakens the original anisotropic composite strength, the primary weakness of commercial laminates remains the stiffness in the third, out-of-plane direction. Instead, natural composites utilize unique orientation of its inorganic reinforcement to provide significant 3-D strength not typical in manufactured composites. If discontinuous fibers can be deliberately aligned within a composite, then isotropic reinforcement similar to these natural systems becomes a possibility.

RESULTS AND DISCUSSION: Here we present our recent characterization of an ultra-high response of Al_2O_3 platelets under magnetic fields. To achieve this response we modify the platelets

first with $<0.1\%$ Fe_3O_4 nanoparticles. This modification allows for the remote control of particle orientation under magnetic fields that can, among numerous exciting possibilities, lead to platelet alignment that can mimic the structures in natural systems. We have developed an energy model for these particle suspensions that explain this ultra-high response and suggest the key parameters essential in these systems. To help validate these parameters, we employed this model in suspensions of rods and successfully predicted the best size regime for high responsiveness. We extend this model to describe the exciting alignment of the platelets second major axis under rotating magnetic fields. We have found a relationship between the viscosity of the suspension and the critical frequency required to change from 'phase-locked' to 'fully-aligned' modes. Finally, we use these techniques to create a family of advanced composites (Fig 1.) exhibiting 3-d reinforcements, spatial gradients, and various deliberate alignments. These composites exhibit the 3-D reinforced structures predicted to have enhanced material properties, such as higher stiffness and 'wear-free' characteristics.

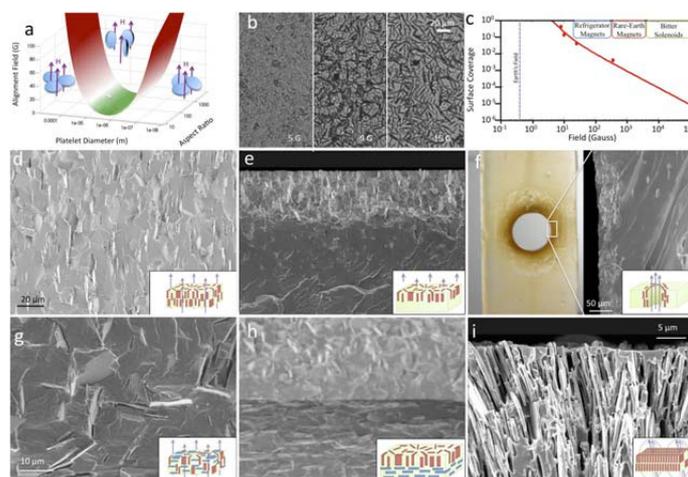


Fig. 1: a) Energy model explaining ultra-high magnetic response. b) Micrographs showing particle alignment at very low magnetic fields as predicted in c). d-i) Various alignment possibilities demonstrated with this method including d) out-of-plane, e) surface concentrated, f) spatially concentrated, g) mixed alignment, h) laminated, and i) under rotating field.

REFERENCES: ¹ R.M.Erb, R. Libanori, N. Rothfuchs, A. R. Studart, In Submission to Science 2011

ACKNOWLEDGEMENTS:

We thank T. Tervoort, L. van Breemen, K. Feldman, M. Imhof, J. Hofstetter, R. Stahel, R. Ehrbar, P. Zweifel, B. Wegmann, M. Schinhammer for their kind experimental assistance, and Antaria Limited, Huntsman Advanced Materials, Rosen and BASF for kindly supplying alumina platelets, polymers and resins. The authors also acknowledge internal funding from ETH Zurich and the Swiss National Science Foundation (grant 200021_135306/1), as well as support by the Electron Microscopy Center of ETH Zurich (EMEZ)

Magnetically Actuated Emulsions Systems

R. Erb¹, J. Sander¹, C. Denier¹, A.R. Studart¹

¹ *Complex Materials, ETH Zürich, Zürich, Switzerland.*

INTRODUCTION: Using magnetic manipulation strategies to handle and control emulsion droplets has been proven to be a good tool for handling and targeting small amounts of material [1,2]. Applying an external magnetic field on paramagnetic emulsion droplets or particles induces an effective magnetic dipole moment in each individual droplet. This dipole field generates magnetic field gradients that cause the particles to chain and presses them together. With high fields, the magnetic force can overcome the stabilizing effects from the surfactant and induce droplet fusion.

Most examples for magnetophoretic transport and controlled release have so far been restricted to structures above 1 mm and fluid loadings in the microliter range [1,2]. At these scales there is no clear benefit of magnetic over manual handling. Instead, we present a method to produce and magnetically manipulate sub mm single and multiple emulsions that offers controlled handling of nL size fluids. Emulsions are made in micro capillary devices and contain magnetic ferro fluid in any one of the dispersed phases. By applying a magnetic field, the emulsion droplets can be manipulated and programmably fused with each other or the continuous phase, resulting in release of their encapsulant.

METHODS: Monodisperse double (water in oil, w/o/w) and single (oil in water, o/w) emulsions were produced in microfluidic glass capillary devices. Most studied systems were either an olive oil or an oil-based ferrofluid, respectively for o/w/o and o/w, dispersed in an aqueous phase sometimes with surfactant. The encapsulated water phase was pure water or aqueous ferrofluid. Droplets were fused using fields between 10 and 150 Gauss. For o/w emulsions, the fusion field was controlled by the addition of 0.01M-0.1M CaCl₂.

RESULTS: To investigate magnetically-triggered droplet fusion, o/w emulsions were produced and collected. In pure water, the droplets chained upon applying a magnetic field and remained stable even at fields up to 60 Gauss. The addition of CaCl₂ works to screen the electrostatic repulsion of the surfactant in the oil phase. At moderate salt concentrations and fields, chains remain stable, but further increases lead to droplet fusion/destruction.

Additionally, double emulsions enable protection of an encapsulant from the continuous phase.

Double emulsion containing aqueous ferrofluid in the inner most phase and olive oil with surfactant in the middle phase are stable at low magnetic fields and can be transported along a magnetic field gradient (Fig 1a) or chained (Fig 1b). Further increase results in release of their cargo (Fig 1c).

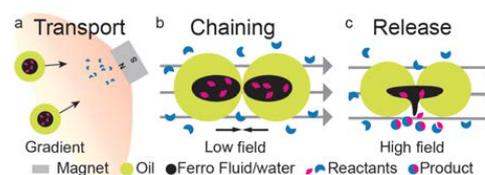


Figure 1: Schematic of (a) transport, (b) chaining and (c) release of w/o/w double emulsions containing ferrofluid in the inner most phase.

Fig 2 shows w/o/w emulsions before and after destruction in a 0 wt% and 2 wt% polyacrylic acid (PAA) aqueous solution. Without PAA, the ferrofluid slowly diffuses into the continuous phase. Instead, the release of cationic ferrofluid in 2wt% PAA leads to gelling of the PAA as evident from the heterogeneous gelling patterns in Fig 2d.

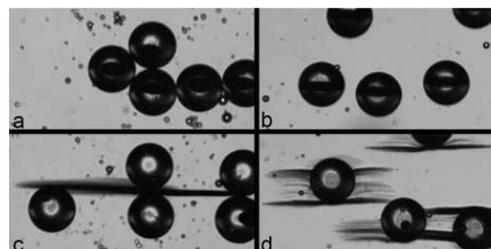


Fig. 2: w/o/w emulsion with aqueous ferrofluid in the inner most phase at (a, b) low and (c,d) high external magnetic fields in a (a, c) 0 wt% and (b,d) 2wt% PAA continuous aqueous phase.

CONCLUSIONS: Here we produce single and double emulsions that are magnetically responsive. We further demonstrate that we can use magnetophoretic techniques to transport, assemble, and programmably rupture these droplets. This allows for the controlled spatial and temporal release of nanoliter-sized encapsulated reactants.

REFERENCES: ¹ T. Lin; **2010**; *Adv. Mater.*; 311 (1):238-243.

² J.R. Dorvee; **2004**; *Nature Mat.*; 3: 896-899.

Three Dimensional Flow of Colloidal Glasses

[T.F.F. Farage](#), [J.M. Brader](#)

¹ *University of Fribourg, Fribourg, Switzerland*

Recent experiments performed on a variety of soft glassy materials have demonstrated that any imposed shear flow serves to simultaneously fluidize these systems in all spatial directions [Ovarlez et al. (2010)]. When probed with a second shear flow, the viscous response of the experimental system is determined by the rate of the primary, fluidizing flow. Motivated by these findings, we employ a recently developed schematic mode-coupling theory [Brader et al. (2009)] to investigate the three dimensional flow of a colloidal glass, subject to a combination of simple shear and uniaxial compression. Despite differences in the specific choice of superposed flow, the flow curves obtained show good qualitative agreement with the experimental findings and recover the observed power law describing the decay of the scaled viscosity as a function of the dominant rate. We then proceed to perform a more formal analysis of our constitutive equation for general 'mixed' flows consisting of a dominant primary flow subject to a weaker perturbing flow. Our study provides further evidence that the theory of Brader et al. (2009) reliably describes the dynamic arrest and mechanical fluidization of dense particulate suspensions.

REFERENCE: [T.F.F. Farage and J.M. Brader, arXiv:1109.0552v1](#) [cond-mat.soft]

G. Ovarlez, Q. Barral, and P. Coussot, Nature Materials, 9, 115-119 (2010)

J.M. Brader, T. Voigtmann, M. Fuchs, R.G. Larson, and M.E. Cates, Proceedings of the National Academy of Science, 106, 15186-15191 (2009)

Rheology modifying cement admixtures

L. Ferrari^{a, b, 1}, *J. Kaufmann*^{a, 1}, *F. Winnefeld*^a

^a Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Concrete/Construction Chemistry, Ueberlandstr. 129, 8600 Dübendorf, Switzerland.

^b Technische Universität München, Department of Chemistry, Lichtenbergstr. 4, 85747 Garching, Germany

¹ Corresponding author: lucia.ferrari@empa.ch

INTRODUCTION

Polycarboxylate ether-based superplasticizers (PCEs) are usually applied in cement technology to improve the rheological properties of fresh and hardening concretes and mortars. In this work we studied the rheology of different kinds of cement, comparing the results with inter-particle force measurements performed by means of atomic force microscopy (AFM).

MATERIALS

Cements: two cements were selected with different tricalcium aluminates content in order to detect the influence of formation of ettringite $(CaO)_3(Al_2O_3)(CaSO_4)_3 \cdot 32H_2O$ on cement rheology. It was found that they form Cem N=3% and Cem HS=1% of ettringite. Cement clinker surface was also applied to detect the dispersion forces occurring on different cement phases.

Polycarboxylate superplasticizers (PCE):

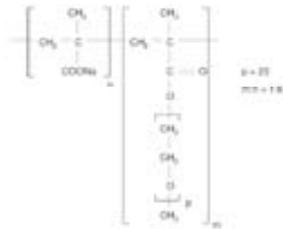


Figure 1: chemical composition of PCE.

METHODS

Rheology: Apparent yield stress was estimated from rheology measurements applying the Bingham method (see figure 2). The two cements were mixed at a water-to-cement ratio of 0.36, the PCE were added in dosage of 1 mg of PCE / g of cement.

Atomic force microscopy (AFM): surface forces were detected by AFM on different clinker phases: ettringite and calcium silicate. The application of a negatively charged sharp tip distinguished between attractive or repulsive forces.

RESULTS

Figure 2 shows cement flow curves in presence and absence of PCE. The main effect of PCE is to reduce the apparent yield stress required to make the cement paste flowing.

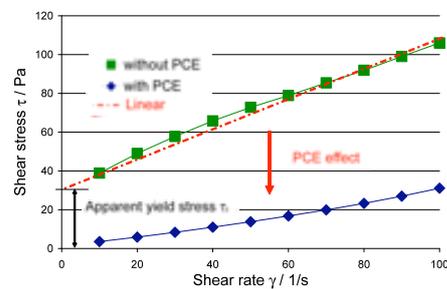


Fig. 2: Effect of PCE on cement rheology.

Figure 3 shows the dispersion forces in presence and absence of superplasticizer on ettringite crystal. When PCE are in solution, dispersion forces are detected.

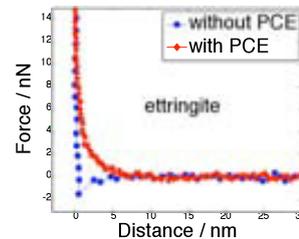


Fig. 3: Force distance measurements on ettringite crystal in presence and absence of PCE.

DISCUSSION & CONCLUSIONS

The addition of PCE to cement paste decreases the apparent yield stress of the mixture. Surface forces were detected to be attractive in absence of PCE, and otherwise repulsive.

REFERENCES

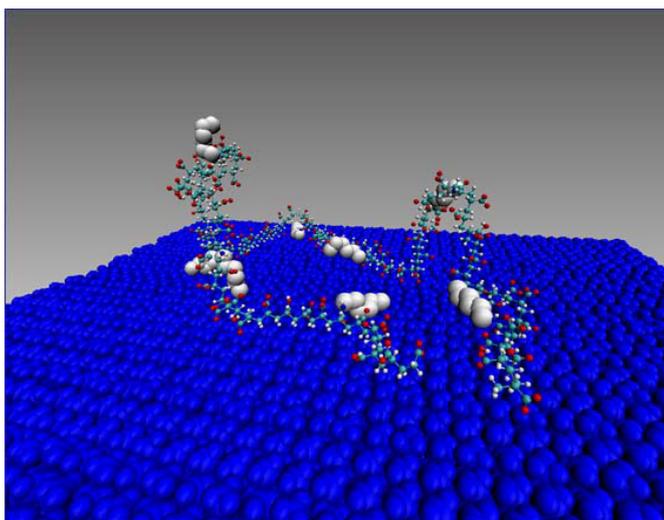
L. Ferrari et al 2011; Cement Concrete Research 41 pp. 1058-1066.

ADSORPTION BEHAVIOUR AND LUBRICATING PROPERTIES
OF AMPHIPHILIC POLYMERS

Giacomo Fontani, Rowena Crockett, Roberto Gaspari,
Daniele Passerone, Nicholas Spencer

ETH Zurich, Surface Science & Technology, Wolfgang-Pauli-Str. 10, 8093 Zurich,
Switzerland

The ability of amphiphilic polymers to self-assemble and form a gel-like layer has been investigated. Experimental studies on a derivative of poly(acrylic) acid (PAAAm) have been performed to understand the relationship between amphiphilic polymer chemistry, structure, water retention and friction between hydrophobic surfaces. The results suggest that PAAAm forms a water-enriched adsorbed layer at hydrophobic surfaces that has got the ability to lower the friction between surfaces. Computational studies on PAAAm have been also performed to better understand hydrogen-bonding interactions and adsorbed conformations. The results suggest that the adsorption process leads to a partially adsorbed molecule, with a small number of hydrophobic side chains pointing into the bulk water, confirming a gel-like layer formation.



Magnetically-assisted structural control of porous silica monoliths

M. Furlan, D. Parakkal, M. Lattuada

Institute for Chemical and Bioengineering, ETH Zürich, Zürich, Switzerland.

INTRODUCTION. The production of porous materials with a well organized structure, for applications such as chromatography, membrane separation, catalyst supports, and scaffolds for cell growth is a challenging problem.

METHOD. We present here a method to create porous silica materials with a complex porous structure. The method makes use of magnetic-polymer nanocolloids, synthesized via free radical miniemulsion polymerization, as templates for the formation of silica monolith via sol-gel process. When an aqueous dispersion of nanoparticles is mixed with a silica precursor, a catalyst and a porogen, silica nucleates and condenses on top of the nanoparticles. However, the spatial arrangement of these nanoparticles can be controlled by means of a magnetic field. When a uniform field is applied, the resulting material has a fibrous structure aligned in the direction of the field. Monoliths with a more complex morphology can be prepared using time dependent configuration of the magnetic field applied during the sol-gel process. The sol-gel process kinetics has first been investigated by means of rheology, in order to precisely identify the gel time. Then, simple time dependent configurations of magnetic field have been applied, such as applying the magnetic field for a time shorter than the gel point, and let complete the reaction without any magnetic field, or starting the reaction in the absence of a field, which was then turned on before the gel point. An additional variation of the procedure has been explored, in which the reaction is started in the presence of a magnetic field, and the sample has then been subjected to strong mixing before allowing the system to percolate in the absence of a field. We have also explored the application of rotating magnetic field, in order to generate materials with two dimensional sheetlike structures in the plane of rotation.

RESULTS. Our strategy aims at controlling the structure through a competition between magnetic dipolar interactions, which align the nanoparticles into strings, and diffusion, shear forces, or rotation, which disrupt the alignment and change the orientation of the strings. A few examples illustrating the variety of structures that be obtained can be obtained are shown in Figure 1.

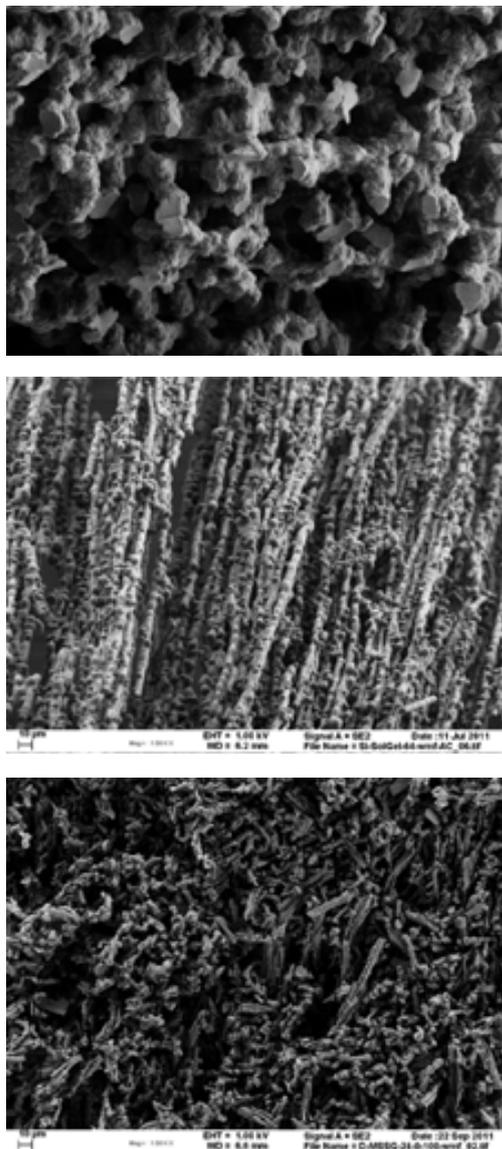


Fig. 1: SEM pictures of typical silica monolith obtained in the absence of a magnetic field, (above), in the presence of static magnetic field (middle) and in presence of magnetic field applied only at the beginning of the sol-gel process (below).

*Effect of viscosity ratio, film drainage time and emulsifier type on avalanches
of coalescence events in emulsion*

Deniz Z. Gunes, Mathilde Bercy

Nestlé Research Center, Vers-chez-les-Blanc, Lausanne 26, CH-1000, Switzerland

The destabilization of emulsions and foams due to coalescence is an important issue regarding the stability of industrial products e.g. in the food industry. Recently, avalanches of coalescence events driven by capillary shape relaxation were reported for water-in-oil emulsions. The first event was induced using a microfluidic or a millifluidic device, where the local external flow tended to separate adjacent drops [1-3]. In the present work, in addition to the geometry of the main channel hosting the flow of drops, side-channels placed laterally to the main channel were used to control inter-drop collisions and separations [4]. The first coalescence event and the occurrence of avalanches was then studied as certain parameters were varied, i.e. the viscosity ratio of the water to the oil phase, the contact time between adjacent drops after collision, and the concentration and the type of surfactant used. Systematic variation of the viscosity ratio was carried out using Newtonian polydimethylsiloxane fluids and mixtures of water with glycerine. At high flow rates from the lateral channels to separate adjacent drops, it was possible to separate them without triggering coalescence. The critical hydrodynamic stress needed to avoid coalescence and the probability of avalanche occurrence both increased, as the contact time between drops was increased, i.e. as the drainage of the lubricating film proceeded during a longer time. The occurrence of avalanches was observed for viscosity ratios in the range 0.001 – 10. Emulsifiers soluble in the water phase appeared not to prevent the avalanche propagation, except for very high interfacial viscosity. In the presence of an emulsifier in the oil phase, the viscosity ratio appeared to be an important parameter regarding the avalanche propagation. Recent experimental results using an AFM apparatus, shed light on how coalescence can occur as two drops are pulled apart, and were in agreement with simulation results [5].

[1] Clain X., Master's thesis, Univ. Paris VI, France/Nestlé Research Center, Lausanne, Switzerland (2007).

[2] Bremond N., Thiam A.R., Bibette J., Phys. Rev. Lett. 100, 024501 (2008).

[3] D.Z. Gunes, X. Clain, O. Breton, Guy Mayor, A.S. Burbidge, J. Coll. Int. Sci. 343, 79 (2010).

[4] Bercy M., Master's thesis, Univ. Paris VI, France/Nestlé Research Center, Lausanne, Switzerland (2010).

[5] Vakarelski I.U., Manica R., Tang X., O'Shea S.J., Stevens G.W., Grieser F., Dagastine R.R., Chan D.Y.C., Proceedings of the National Academy of Sciences of the United States of America 107 (25), 11177 (2010).

Regularized Landau-de Gennes free energy for nematics

Patrick Ilg

Polymer Physics, ETH Zürich, Wolfgang-Pauli Str. 10, CH-8093 Zürich

The Landau-de Gennes free energy plays a central role in the macroscopic theory of anisotropic fluids [1]. In its original formulation, however, the Landau-de Gennes free energy is valid only close to the phase transition and should not be used naively in nonequilibrium situations [2]. Here, we derive first the ideal, entropic contribution to this free energy, that is always present in these systems, irrespectively of the detailed form of interactions or applied fields. An explicit and compact form of the macroscopic, ideal entropy is derived and successfully tested [3]. This entropy is nonpolynomial in the order parameter, diverging logarithmically near the fully oriented state and therefore restricting the order parameter to physical admissible values. In a second step, we show how this derivation can be extended for more realistic microscopic models. As an application, it is shown that the isotropic-nematic transition within the Maier-Saupe model is described in a simple, yet very accurate manner.

References

- [1] P. G. de Gennes, J. Prost, *The Physics of Liquid Crystals* (Oxford 1993).
- [2] A. Majumdar, *Europ. J. Appl. Math* 21, 181 (2010).
- [3] P. Ilg, M. Hütter, M. Kröger, *Phys. Rev. E* 83, 061713 (2011).

From Powders to Collapsible Structures/"Living Quicksand": Discrete Modeling

D. Kadau¹, H. J. Herrmann¹

¹ ETH Zurich, Zurich, Switzerland.

The discrete element method constitutes a general class of modeling techniques to simulate the microscopic behavior (i.e., at the particle scale) of granular/soil materials. We present a variant of the contact dynamics method, originally developed to model compact and dry systems with lasting contacts. This variant accounts for the cohesive nature of fine powders and soils and can be used in various applications [1].

We use a modification of the model to investigate the "quicksand" behavior of a collapsing soil/suspension material. Our model is validated with real data obtained from in situ measurements performed with a specific type of natural quicksand at the shore of drying lagoons showing a yield-stress material behavior [2-3]. We also investigate how deep an object can be pushed in and how well the intruder is captured by the material after it collapsed above the intruder. During the penetration process we measured the relation between the driving force and the resulting velocity of the intruder [4]. We also investigated the influence of different strength of viscous drag acting on the grains [1].

The loose granular structures involved in collapsing soils/suspensions and many other materials are investigated in detail. We study the influence of the granular bond number on the density profiles and the generation process of the loose packings, in our case a ballistic deposition process while at the same time the structures collapse due to gravity. This collapse occurs discontinuously in slides which are the basis for developing a model for the final density profiles [5].

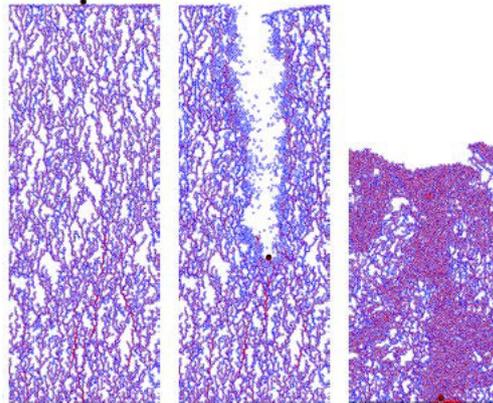


Fig. 1: Snapshots from computational simulations showing a typical realization of the penetration process of an intruder into a very loose cohesive packing. The (unperturbed) collapsing suspension/soil is shown left. As shown in the middle the movement of the intruder is responsible for the partial destruction of the granular structure along its trajectory. At the end (right), the intruder rests under a compact mass of (perturbed) material.

REFERENCES:

- [1] D. Kadau. *From Powders to Collapsing Soil/Living Quicksand: Discrete Modeling and Experiment*. AIP Conference Proceedings 1227, 50-57 (2010).
- [2] D. Kadau, H.J. Herrmann, J.S. Andrade Jr., A.D. Araujo, L.J.C. Bezerra, L.P. Maia, *Living Quicksand*, *Granular Matter* 11, 67-71 (2009)
- [3] D. Kadau, H.J. Herrmann, J.S. Andrade Jr., *Collapsing granular suspensions*, *Eur.Phys.J.E* 30, 275-281 (2009)
- [4] D. Kadau, H.J. Herrmann and J.S. Andrade Jr. *A micromechanical model of collapsing quicksand*, *Granular Matter* 13(3), 219-223 (2011), Special Issue in memory of I. Vardoulakis.
- [5] D. Kadau, H.J. Herrmann. *Density profiles of loose and collapsed cohesive granular structures generated by ballistic deposition*. *Physical Review E* 83, 031301 (2011)

*Atomic Force Microscopy as a Tool to Investigate the
Properties of Polyglycerol Ester Foams*

*R. Keller**, *C. Curschellas*[°], *R. Berger**, *U. Rietzler**, *D. Fell**, *H.J. Limbach*³, *H.-J. Butt**

**Max-Planck-Institute for Polymer Research, 55122 Mainz, Germany*

°Laboratory of Food Process Engineering, ETH Zürich, 8092 Zürich, Switzerland

³Nestec Ltd., Nestlé Research Center, 1000 Lausanne 26, Switzerland

Abstract:

Foamed products are a very popular class of food products. The stabilization mechanism of air bubbles within such foams is often only partially understood. The current study aims at better understanding the stabilization of air-water interfaces through the low molecular weight surfactant polyglycerol ester (PGE). To reach this goal several different film preparation methods have been tested. The produced films were then investigated by atomic force microscopy (AFM) in order to elucidate the film structure and thus the stabilizing mechanism. In addition to the study of Langmuir monolayers and Gibbs adsorption layers, we have proposed a new approach to investigate the skins of foam bubbles. We were able to show that a combination of these different film preparation methods can give a good overview over the different properties of air-water interfacial films.

CW and Pulse EPR Spectroscopy on Polymer-Clay Nanocomposites

[U.Kielmann](#)¹, [I.GarciaRubió](#)¹, [E.Barthazy](#)², [A.Bittermann](#)², [G.Jeschke](#)¹

¹Laboratory of Physical Chemistry, ETH Zürich, Zürich, Switzerland.

²EMEZ, ETH Zürich, Zürich, Switzerland.

INTRODUCTION: In recent years polymer clay nanocomposites gathered a considerable interest in polymer science as well as industry because of improvements of their properties compared to polymers without clay [1]. Although a lot of work was published, there still exists poor knowledge about their nanoscale structure responsible for the material characteristics.

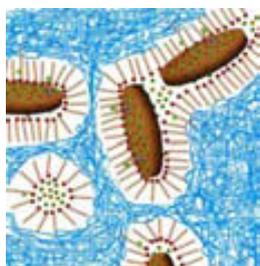


Fig. 1: Possible structure of polymer clay-nanocomposites - CAT1 spin probes can be addressed to the clay surface, SSD can be incorporated into the SDS-micelle.

METHODS: EPR spectroscopy was used to resolve the structure of weakly ordered materials like polymer-clay nanocomposites in a nanoscale range by probing the environment with stable nitroxide molecule radicals [2,3]. Specific spin probes are sensitive to the interaction between clay particles and polymer particles in dispersion, which allows to study different sites in the system. With two-dimensional pulse EPR spectroscopy like HYSCORE it is possible to study hyperfine interaction between the electron spin and the nuclei, which gives us information about geometry and distances up to few nanometers in this system.

RESULTS: It was possible to incorporate SSD (5-DOXYL-stearate) into the SDS-micelles of the polymer and to address the clay surface with the cationic probe CAT1 (4-trimethyl-ammonium-2,2,6,6-tetramethylpiperidine). The HYSCORE spectra of the probed regions show different ²³Na nuclei with distinct distance distributions (Fig. 2). It could be shown that the clay particles are embedded in an ionic environment in the nanocomposite.

DISCUSSION & CONCLUSIONS: HYSCORE spectroscopy is sensitive to the nanoscale environment of the spin probe. A distinct ²³Na

signal could be detected addressing specific regions with different nitroxide probes. The signals have to be assigned to a distance distribution of nuclei. A proper model has to be applied to get more structural information about ionic regions interacting with clay and the polar groups of SDS in nanocomposites.

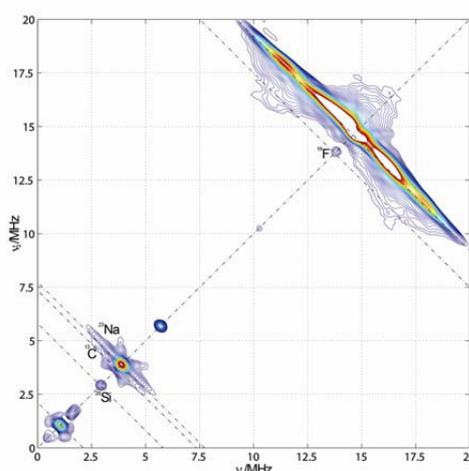


Fig. 2: HYSCORE spectrum of the microenvironment of CAT1, selectively addressed to the clay surface of the composite.

REFERENCES: ¹S. Ray, M. Okamoto; 2003; *Prog. Polym. Sci.*; 28:1539.

²S. Cramer, G. Jeschke, H. Spiess; 2002; *Macromol. Chem. Phys* 203:182.

³S. Cramer, G. Jeschke, H. Spiess; 2002; *Macromol. Chem. Phys*; 203:192.

ACKNOWLEDGEMENTS: Differential Scanning Calorimetry – Dr. Paola Luciani, Institute of Pharmaceutical Sciences, ETH Zürich, Switzerland

Polymer dispersions – Polymer Latex GmbH Marl, Germany

Laponites – Rockwood Additives Ltd Widnes, United Kingdom

Somasif-ME 100 – CO-OP Chemical Co Ltd Tokyo, Japan

Photo-responsive reversible aggregation and dissolution of rod-like polypeptide diblock copolymers

Venkata Krishna Kotharangannagari^{†,‡}, Antoni Sánchez-Ferrer[‡], Janne Ruokolainen[§], and Raffaele Mezzenga^{*,‡}

[†] Department of Physics and Frimat Center for Nanomaterials, University of Fribourg, Chemin du Musée 3, 1700 Fribourg, Switzerland.

[‡] Food & Soft Materials Science, Institute of Food, Nutrition & Health, ETH Zurich LFO-E-23, Schmelzbergstrasse 9, 8092 Zurich, Switzerland.

[§] Department of Applied Physics, AALTO University, P.O. Box 15100, FIN-00076, Helsinki, Finland.

INTRODUCTION: Polypeptides are attractive in the biomedical field due to their unique protein-mimetic properties.¹ Light-responsive polypeptide block copolymer systems capable to undergo reversible micellization could target unchallenged potential applications not only in the biomedical, but also in the drug delivery area due to the desirable combined effect of non-invasive stimuli-responsiveness and biocompatibility. Available state of the art in the field is encouraging to pursue such an effort: it is well known that poly L-glutamic acid solutions containing spiropyran as side-chain motif can undergo conformational changes (from α -helix to random coil and vice versa) with UV and visible light, respectively.²

METHODS: UV-Vis spectroscopy, Cryogenic transmission electron microscopy (cryo-TEM) and circular dichroism (CD).

RESULTS:

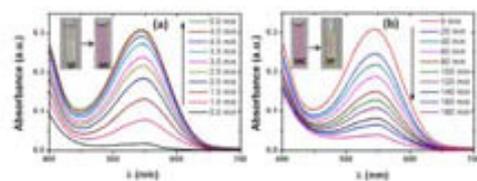


Fig. 1: (a) Photo-isomerization process for a 0.01 wt-% of PLGASP₂₀-b-PEO₄₆₀ in solution with UV light ($\lambda = 350$ nm) irradiation, and (b) back photo-isomerization process with visible light ($\lambda = 590$ nm) irradiation.

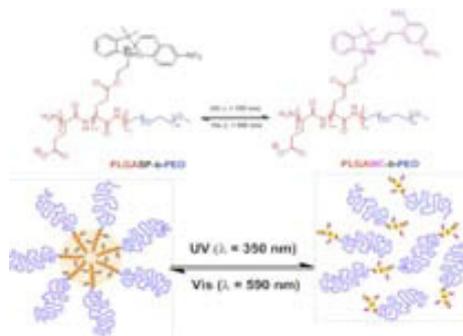


Fig.2: Schematic illustration of photo-responsive micellization/dissolution process for the PLGASP-b-PEO block copolymer studied in this work.

DISCUSSION & CONCLUSIONS: We have shown a new pathway to the use of polypeptide block copolymers as robust light-responsive systems, capable to undergo a reversible aggregation-dissolution-aggregation process in water solutions in response to a suitable light exposure history. Because the stimulus used here is a non-invasive highly penetrating UV source and the block copolymers have a bio-inspired molecular architecture, these photo-responsive rod-coil block polypeptide can be used as viable model systems to study photo-induced drug release processes or light-controlled biomedical applications.

REFERENCES: ¹ Carlsen, A.; Lecommandoux, S. *Current Opinion in Colloid & Interface Science* 2009, 14, 329 - 339.

² Ciardelli, F.; Fabbri, D.; Pieroni, O.; Fissi, A. *Am. Chem. Soc.* 1989, 111, 3470-3472.

³ Kotharangannagari, V.; Sanchez-Ferrer, A.; Ruokolainen, J.; Mezzenga, R. *Macromolecules* 2011, 44, 4569-4573.

A new level of structural control on amyloid fibrils: self-assembled lysozyme

C. Lara, I. Usov, J. Adamcik, S. Jordens, R. Mezzenga
ETHZ, Zürich, Switzerland

INTRODUCTION: Most proteins can form amyloid fibrils, which are supramolecular fibrillar aggregates, *in vivo* or *in vitro*, leading to neuronal and systemic pathologies. Hen egg white lysozyme (HEWL) is a typical example of globular protein which can form amyloid fibrils and can cause cell death under specific conditions. However, no reports have tackled systematically the molecular configurations of lysozyme fibrils at various length scales or drawn general conclusions on the fibrillation process of this model protein.

We use single-molecule atomic force microscopy statistical analysis and polymer physics concepts to show that different incubation conditions can lead to two different structural assemblies. The first structure can be described as multi-stranded helical ribbons with cross-sectioned growth progressing up to unprecedented levels [1]. The second one corresponds to sinusoid-like fibrils conformation that can be described with polymer physics concepts with a complex scaling behavior varying at multiple length scales. We use bond and pair correlation functions, end-to-end chain distribution and worm-like chain model to identify three characteristic length scales corresponding to the bending length L_b , the period P and the persistence length L_p .

METHODS: Solutions of 2% w/w dialyzed protein were prepared in Milli-Q water at pH 2 and incubated at 60°C or 90°C for several days. Formation of amyloid aggregates was detected as enhancement of the ThT fluorescence intensity. Fibrils were imaged by tapping mode AFM, Cryo-TEM and TEM. SDS-PAGE was run and Far-UV CD spectra were recorded to follow structural changes.

RESULTS:

While the “wavy” fibrils obtained at 60°C are well described by a SAW at length scales larger than the persistence length (μm), a characteristic undulating periodicity appears at lower length scales ($P \approx 250\text{nm}$), which can be used to model the fibril as a pseudo-sinusoid. At even lower length scales ($< \frac{1}{2} P$), called bending length scale, the fibrils become rod-like again and recover a one-dimensional behavior. The topological features of the sinusoid-like fibrils are interpreted to arise from a twisting anisotropic cross-section combined with thermal bending energy. At 90°C

however, a totally different structure is observed, corresponding to helical ribbons with a number of filaments increasing with incubation time up to 17 and a cross section 173 nm wide. These results are interpreted as a consequence of the simultaneous protein unfolding, hydrolysis into very short fragments and fibrillation. These results are supported by circular dichroism and SDS-page analysis.

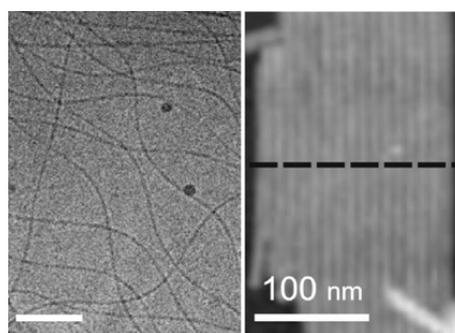


Fig. 1: Cryo-TEM and AFM height images of HEWL incubated at 60°C (left) and 90°C (right).

DISCUSSION & CONCLUSIONS:

These results open new perspectives in the understanding of fibrillation processes in globular proteins and amyloids polymorphism. Experimental results provide convincing evidence that protein unfolding and complete hydrolysis are essential for the formation of large laminated aggregates. The exceptional similarities in the fibrillation steps, building blocks and final amyloid structures for globular proteins as diverse as lactoglobulin (used as a benchmarking) and lysozyme and the direct analogies with aggregation processes in short synthetic polypeptides, further support a possible general common unfolding-fragmentation-aggregation mechanism for amyloidosis in globular proteins. Furthermore, the diversity of structures observed for HEWL underlines the decisive role of the incubation conditions.

REFERENCES: C. Lara, J. Adamcik, S. Jordens, R. Mezzenga; 2011; *Biomacromolecules*; 12:1868-1875.

ACKNOWLEDGEMENTS: We thank S. Handschin for support with cryo-TEM imaging.

LIQUID TRANSPORT IN SHEARED WET GRANULAR MATTER

R. Manl¹, D. Kadau¹, H.J. Herrmann¹
¹ ETH Zürich, Zürich, Switzerland.

INTRODUCTION: *Where does liquid migrate in shear bands formed in wet granular matter? It is known that in fully saturated granular media the liquid content increases in dilating shear bands. However, it is not clear what happens at low liquid contents. Also, mixing of liquid and granular matter is of great importance, e.g. in powder technology or pharmaceutical applications. Here, we present a microscopic model for liquid transport at low liquid contents, where the volume of a ruptured bridge is redistributed to neighboring bridges. When shearing wet granular media, liquid is also redistributed on large scales. We describe how a homogeneous liquid distribution can turn inhomogeneous and vice-versa.*

METHODS: *We use contact dynamics to model spherical particles interacting via Coulombian friction as well as via cohesive capillary forces. The contact forces are determined by means of constraints and are computed iteratively in each time step. The cohesive force is calculated as a function of the separation of the particles and the bridge volume.*

RESULTS: *We derived a modified diffusion equation describing the liquid transport in sheared granular matter. It predicts that liquid is driven out of shear bands despite the increased porosity due to dilatancy. Furthermore, it describes how inhomogeneous liquid distributions evolve in time. Fig. 1 shows a wet granulate in periodic simple shear. It is sheared between two rough walls by applying a constant pressure P on the upper wall and the lower wall is moving with constant speed. Periodic boundary conditions are imposed in the shear direction. Initially, there is a slice of liquid bridges in the middle of the sample indicated by the blue (dark) lines. We observe that liquid spreads towards the upper and lower wall. This redistribution of liquid depends on the local liquid content as well as on the local shear rate. We found that liquid is driven away from regions of high shear rates towards regions of lower shear rates. A convenient set up to study such inhomogeneous shear rate profiles is the linear split bottom geometry. It exhibits a stable shear band at fixed position and we found that liquid is driven out of the shear band.*

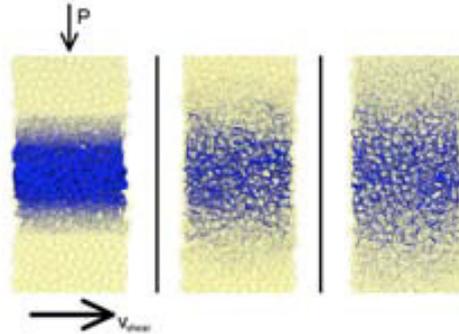


Fig. 1: A periodically sheared granular sample between two rough walls. Left: Beginning of the simulation with a Gaussian distribution of liquid bridge volumes (blue/dark lines). Middle and right: Subsequent snapshots of the simulation. The liquid spreads towards the top and bottom walls.

OUTLOOK: *Future experiments, e.g. in a circular split bottom shear cell should be performed in order to verify our results.*

ACKNOWLEDGEMENTS: *We thank Martin Brinkmann and Dani Or for helpful discussions.*

Dynamics and ordering of ellipsoidal nanoparticles: from low to high volume fractions

Ilya Martchenko^{1,2}, Jérôme J. Crassous^{1,2}, Chantal Rufie³,
Hervé Dietsch¹, Mathias Reufer⁴, and Peter Schurtenberger²

¹ University of Fribourg, Fribourg, Switzerland. ² Lund University, Lund, Sweden.

³ INSA de Lyon, Villeurbanne, France. ⁴ University of Edinburgh, Edinburgh, UK.

INTRODUCTION: Tailor-made nanoparticles are promising model systems, as their characteristic time and length scales are easily accessible with experimental techniques of colloidal physics. The anisotropic colloids attract growing interest as they can be well suited to study dynamics and phase behaviour of real non-spherical systems. Such applications require, however, well-defined particles with a set of adjustable physical features. We establish and characterize nearly monodisperse inorganic ellipsoids with tuneable size, aspect ratio, magnetic, and optical properties. For these particles, we probe the dynamics and structural ordering in suspension via a combination of scattering and microscopy techniques.

RESULTS: The ellipsoids are synthesized via colloidal templating approach by coating a hematite spindle-type core with a uniform layer of silica.¹ The magnetic core (Fig. 1, left) can be removed, yielding non-magnetic capsules (right) with reduced turbidity and negative buoyancy. The size and aspect ratio can be tuned by increasing the thickness of the coating.

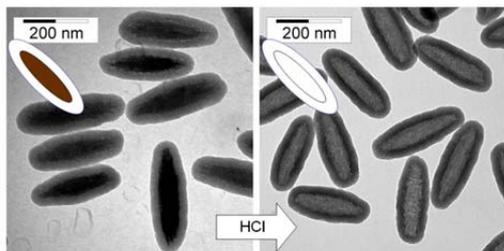


Fig. 1: TEM micrograph: core-shell hematite-silica ellipsoids (left) and silica capsules (right)

In dilute regime, the rotational and translational dynamics of the particles can be compared to simple hydrodynamic models for ideal geometries (ellipsoids.) A combination of TEM-based calculations and measurements with polarized and depolarized light scattering shows quantitative agreement for a range of aspect ratios.

The small-angle X-ray scattering measurements are used to determine the structure factor $S(q)$ at a range of volume fractions. For non-magnetic capsules (Fig. 2) and magnetic particles, SAXS indicates the positional correlations evolving with

the volume fraction. The magnetic field allows further control of the orientation of the magnetic particles, yielding a nematic order at high volume fraction that persists when the field is removed.

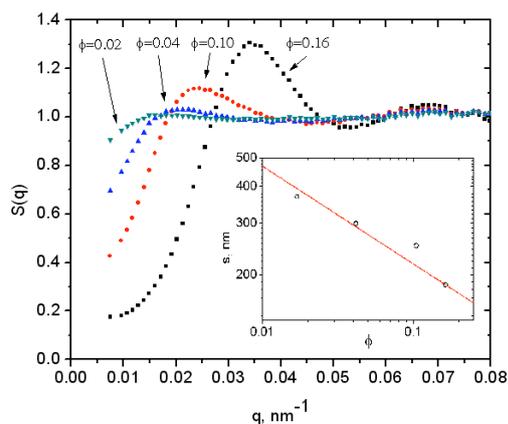


Fig. 2: Structure factors for ellipsoids at growing volume fractions show the increasing positional correlations. The inset shows the characteristic distance $2\pi/q^*$ as a function of volume fraction.

DISCUSSION & CONCLUSIONS: The system is ideal to look at anisotropic colloids which undergo non-isotropic diffusion and interact via non-centrosymmetric potentials. Strong positional and orientational ordering develops at higher volume fractions and can be influenced with the onset of magnetic interactions. These results provide a good position to tackle experimentally the dynamics and phase transitions in the system, and make comparisons to earlier simulations.²

REFERENCES: ¹ I. Martchenko, H. Dietsch, C. Moitzi, P. Schurtenberger; 2011 *J. Phys. Chem. B*; 115: in press, front cover. ² P. Pfliegerer et al.; 2008; *Eur. Phys. Lett*; 84, 1600.

ACKNOWLEDGEMENTS: Adolphe Merkle Foundation, Swiss National Science Foundation, COST action D43, Swiss State Secretariat for Education and Research are gratefully acknowledged for the financial support.

Hydrogels for Control of Cell Morphology and Differentiation

R. Mhanná, J. Becher, M. Schnabelrauch, M. Zenobi-Wong¹

¹ Cartilage Engineering + Regeneration and Lab. for Biosensors and Bioelectronics, ETH Zürich, Switzerland² INNOVENT e.V., Jena, Germany.

INTRODUCTION: Many cell types lose their functionality when grown on tissue culture plastic and other two-dimensional substrates. For this reason, geometry-sensitive cell types are often grown in a 3D environment including pellet culture, hanging drop cultures or within hydrogels. In our research groups, we investigate how the properties of the hydrogels (composition, stiffness, bioactivity, charge) can affect the phenotype and fate of the cells grown within them. In particular we are interested in whether the presence of sulphate groups in the hydrogel can be useful for cartilage engineering.

METHODS: Bovine chondrocytes were isolated from the knee cartilage of 6 month old calves using a pronase/collagenase digestion. Cells were then mixed with a variety of materials and soft hydrogels were formed using the gelation methods outlined in Table 1.

Material	Modification	Gelation
Alginate	Sulfated Alginate, RGD-Alginate	Ca ²⁺
Collagen		Thermal, pH
PEG	RGD, GFOGER peptides	Michael addition
Chondroitin sulfate, hyaluronan	Methacrylate	Photo-crosslinking

RESULTS: Biomaterials can induce a range of cell morphologies, from fully spread to fully rounded (Figure 1). Generally, the former is associated with the induction of the osteogenic/fibroblastic lineage and the latter with chondrogenic differentiation.

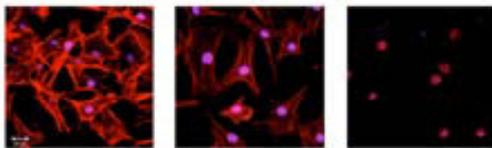
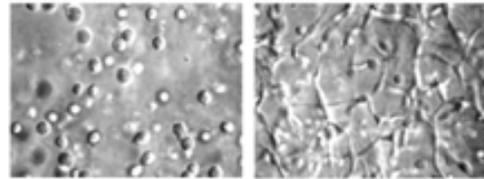


Figure 1: Chondrocytes on tissue culture plastic (left), collagen coating (middle) and in alginate hydrogel (right).

Within three-dimensional gels, the addition of biological moieties can be used by the cells to adhere and attach to the biomaterial. Cells in

100% sulphated alginate become elongated and fibroblast-like in appearance after 4 days of culture (Figure 2)

Figure 2: Bovine chondrocytes display a rounded or spread morphology depending on availability of



sulfation sites.

Finally, in order to further increase the sulphation in the cell's extracellular environment to the maximum extent, we are exploring the use of chondroitin sulphate methacrylates. These gels can be polymerized using a number of photoinitiator systems (Table 2) and may increase the chondrogenic phenotype of the encapsulated cells.

Table 2. Conditions for photocrosslinking methacrylate gels

Photoinitiator	Wavelength
Eosin/ triethanolamine	580
Irgacure 2959	365
VA-086	365

DISCUSSION & CONCLUSIONS: We present a range of tools by which the morphology, and therefore the fate, of biological cells can be controlled. These tools may prove useful in designing therapeutic strategies to treat skeletal injury.

ACKNOWLEDGEMENTS: European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° NMP4-SL-2009-229292 (Find&Bind).

A systematic analysis of protein covered air/water and oil/water interfaces

A. Mütze, V. Mitropoulos, E.J. Windhab, P. Fischer

Institute of Food, Nutrition and Health, ETH Zürich, Switzerland

INTRODUCTION: The proteins bovine serum albumin (BSA), β -lactoglobulin (bLac), and lysozyme are often used in the food industry to stabilize foams and emulsions [1, 2]. They adsorb at the interface and form a stable interfacial film. In order to apply them in a targeted manner with respect to their specific properties, it is necessary to analyze them under comparable conditions. Therefore, we study the protein specific adsorption kinetics and rheological properties of the resulting viscoelastic layer at two different interfaces.

METHODS: The mentioned proteins above were analyzed for various concentrations at an air/water (A/W) and oil/water (O/W) interface, where limonene was used as the oil phase. Adsorption kinetics and dilatational properties of the interfacial layer were determined using a drop profile analysis tensiometer (PAT). Shear rheological measurements were performed during adsorption with a rheometer equipped with a biconical disc.

RESULTS & DISCUSSION: During dilatation a viscoelastic layer with mainly elastic properties is observed throughout. The layers show different discontinuities for both interfaces. Observe that the drop surface shows wrinkles after the dilatation at the O/W interface (see Fig. 1).

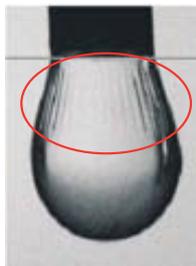


Fig. 1: Camera Image of a pendant drop after dilatation.

At an A/W interface the surface pressure increases more slowly at the beginning of adsorption and the maximal surface pressure is reached earlier in contrast to an O/W interface [2]. For lower concentrations adsorption kinetics decrease and an induction time is measured for all proteins.

At the O/W interface all layers formed show no viscoelastic region during the first hour of adsorption for low concentrations (see Fig. 2)

compare to the A/W interface. Notice that at the O/W interface over time a change from pre-gel like character to rubber-elastic character can be observed. After reaching a maximal surface pressure the layer behavior does not change anymore for both interfaces and the interfacial layer shows rubber-elastic properties.

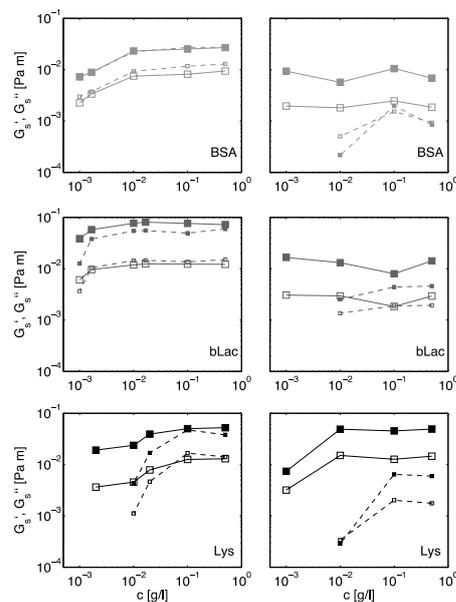


Fig. 2: Interfacial parameters $G'(c)$ (solid symbols) and $G''(c)$ (open symbols) for BSA, bLac and lysozyme at the A/W and O/W interfaces (measurements at the beginning of adsorption (continuous line) and at surface pressure maximum (dashed line); $T = 21.5^\circ\text{C}$, $\text{pH } 7.4$, $\omega = 1 \text{ s}^{-1}$ and $\gamma = 0.221 \%$).

CONCLUSIONS: The adsorption process of each protein and rheological properties of the formed interfacial layer depend on bulk concentration, bulk phase nature, and molecular characteristics such as structure, size, and stability of the proteins.

REFERENCES: ¹ P.Fischer, P.Erni;2007; Curr. Opin. Colloid Sci.; 12:196-205.

² P.Erni, E.J.Windhab, P.Fischer;2011; Macromol. Mat. Eng.; 296: 249-262.

ACKNOWLEDGEMENTS: The authors thank IVU, TU Dresden for cooperation.

How to obtain a galactomannan standard for solution rheology?

M. Pollard, S. Illmann, E.J. Windhab, P. Fischer

Institute of Food, Nutrition and Health, ETH Zurich, Schmelzbergstrasse 9,
8092 Zurich, Switzerland

Water-soluble polysaccharides extracted from legume seed endosperms such as galactomannans and are well known as viscosifiers due to their high molecular weight. The molecular structure has been found to consist of a backbone of mannose with galactose sidegroups at variable degree of substitution according to the specific plant source [1-2]. Galactomannan polysaccharides extracted from seed endosperms of various species have been characterized by size-exclusion chromatography, dilute-solution viscometry, and oscillatory-shear rheology to determine their potential as aqueous thickeners. The molecular composition and chain-length distribution were found to be nearly identical, and thus galactomannans within the same genus are presumed to share a common molecular structure. Obtained scaling properties suggest that in contrast to common belief, water can be considered as a good solvent and therefore the Colby-Rubenstein model can be utilized to describe galactomannan solution rheology [3]. Solutions above the crossover concentration exhibited shear-thinning behavior, and strong dependence of viscosity on concentration. Seed characteristics such as shape, mass, and endosperm content were also assessed, and based on this investigation, some legume endosperms are advantageous for industrial processing and could be adapted for e.g. guar gum replacement [4-6].

- [1] Pollard MA, Fischer P: *Current Opinion in Colloid & Interface Science* 11 (2006) 184-190.
- [2] Pollard MA, Kelly R, Wahl C, Fischer P, Windhab EJ, Eder B, Amado R: *Food Hydrocolloids* 21 (2007) 683-692.
- [3] Colby RH, Rubinstein M: *Macromolecules* 23 (1990) 2753-2757.
- [4] Pollard MA, Kelly R, Fischer P, Windhab EJ, Eder B, Amado R: *Food Hydrocolloids* 22 (2008) 1596-1606.
- [5] Pollard MA, Eder B, Fischer P, Windhab EJ: *Carbohydrate Polymers* 79 (2010) 70-84.
- [6] Pollard MA, Fischer P, Windhab EJ: *Carbohydrate Polymers* 84 (2011) 550-559.

The mechanism of membrane interaction and disruption by α -Synuclein

N.Reynolds¹, A.Soragni², M. Rabe¹, D. Verdes¹, E. Liverani², S. Handshin², R. Riek², S. Seeger¹

¹ University of Zurich, Zurich, Switzerland; ² ETH Zürich, Zürich, Switzerland.

INTRODUCTION: Parkinson's disease is a common progressive neurodegenerative condition, characterized by the deposition of amyloid fibrils as Lewy bodies in the substantia nigra of affected individuals. These insoluble aggregates predominantly consist of the protein α -Synuclein (α -Syn). There is increasing evidence suggesting that the aggregation of α -Syn is influenced by lipid membranes and, vice versa, the membrane integrity is severely affected by the presence of bound aggregates. Here, using the surface sensitive imaging technique supercritical angle fluorescence microscopy (SAF) and Förster resonance energy transfer (FRET) we report the direct observation of α -Syn aggregation on supported lipid bilayers (SLBs). Both the wild-type and two mutant forms of α -Syn studied, namely the familiar variant A53T and the designed highly toxic variant E57K, were found to follow the same mechanism of polymerization and membrane damage. This mechanism involved the extraction of lipids from the bilayer and their clustering around growing- α -Syn aggregates. The process of membrane damage could resemble the yet poorly understood cellular toxicity phenomenon *in vivo*.

METHODS: The adsorption and aggregation of α -Syn onto negatively charged SLBs was monitored by a range of complimentary techniques including SAF, confocal microscopy, and cryo-SEM revealing both aggregate morphology, and integrity of the underlying membrane. To gain insight into how the membrane mediated protein aggregation affected the lateral mobility of the lipids within the SLB, a combination of fluorescence recovery after photobleaching (FRAP) and fluorescence correlation spectroscopy (FCS) was employed. Furthermore, the structure of the resulting protein aggregates was quantitatively analysed by circular dichroism (CD).

RESULTS: Using the experimental methods listed above a number of important results were obtained. First, it was shown using FCS and FRAP that α -Syn molecules interact with the membrane and reduce the lateral mobility of the lipids within. Second, by covalently attaching both lipids and proteins with fluorophores possessing overlapping emission and excitation spectra respectively, it was possible to observe the tight membrane binding of growing α -Syn aggregates by FRET. These

experiments also led to the observation of lipid clustering around the growing aggregates. Furthermore, the ability of the SAF microscope to give accurate information on the 3D structure of the samples revealed that lipids are extracted from the surface of the membrane and transferred to the surface of the growing protein aggregates (Fig. 1).

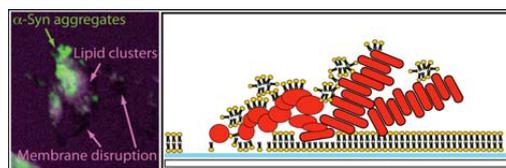


Fig. 1: α -Syn aggregation into amyloid fibrils causes clustering of lipids and leading to membrane disruption.

In order to gain insight into the structure of the membrane bound aggregates, experiments were performed with both fluorescent polythiophene molecules (Fig. 1) and antibodies specific to the cross β -sheet structure ubiquitous in amyloid fibrils. Both experiments gave positive results for the presence of mature fibrils present on the surface of the SLB. In addition, cryo-SEM images were taken to confirm the fibril-like morphology of the α -Syn aggregates. Finally experiments were performed using either aggregation inhibitors or preformed fibers, to determine the conformational species responsible for the observed lipid clustering and extraction.

DISCUSSION & CONCLUSIONS: The conformational species of α -Syn responsible for cytotoxicity in PD is heavily debated. Here it was found that membrane damage only occurs in the presence of aggregating protein when there is a constant supply of monomeric α -Syn. This leads to a new hypothesis that proposes not one species being responsible for cytotoxicity in PD. Instead it is the process of aggregation itself that causes lipid extraction, eventually causing a loss of membrane integrity. As membrane interaction appears to be a principle feature of amyloids, we propose that this mechanism may also be relevant for other amyloid related diseases.

REFERENCES: ¹N. Reynolds et al., J. Am. Chem. Soc., In Press, DOI: 10.1021/ja2029848.

Dilatational Rheology of Protein Fibers at Fluid-Fluid Interfaces

P.A. Rühls¹, S. Danner², S. Jörden², I. Lucio³, E.J. Windhab¹, R. Mezzenga², P. Fischer¹

¹ Food Process Engineering, ETH Zürich, ² Food & Soft Materials, ETH Zürich.

³ Surface Science and Technology, ETH Zürich, Zürich, Switzerland

INTRODUCTION: The mechanical stabilization of a water-air and water-oil interface using modified protein fibers of β -lactoglobulin is investigated experimentally. Protein fibers are obtained by combined pH and heat denaturation of globular food proteins (see Fig.1). These fibers bear many similarities with amyloid fibers, but can be tuned in their shape, flexibility, length and charge density by using various production protocols¹.

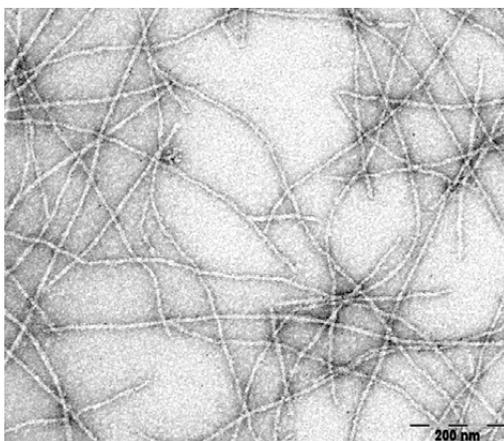


Fig. 1: TEM image of β -lactoglobulin fibrils created through heat and pH denaturation.

METHODS: To address the rheological properties of these fibers at the interface we use interfacial dilatational rheology (pendant drop tensiometry) probing directly the transient evolution of the mechanical properties.

RESULTS & DISCUSSION: The protein fiber aggregation at the interfaces is ruled by both, adsorption and denaturing steps, which eventually lead to a dense adsorption layer. Dilatational rheology show that depending on the adsorption kinetics and experimental time, parameters such as dilatational viscosity and elasticity are corrupted by superimposed protein adsorption. A triangle oscillation (Fig. 2) clearly shows the influence of protein adsorption on dilatational rheological parameters (Fig. 3).

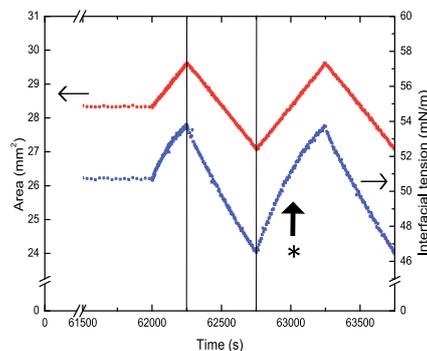


Fig. 2: Triangle oscillations: Bottom line is the response of the interfacial tension to the area (top line). The * indicates the change of the slope.

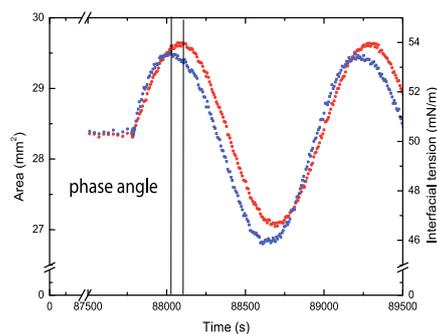


Fig. 3: Interfacial tension (red) response to the area change (blue). The interfacial tension precedes the area change.

A proposition is made to account for the time scales during protein adsorption and mechanical deformation.

REFERENCES: ¹ J. M. Jung, D.Z. Gunes, R. Mezzenga; 2010; Langmuir 26:15366-15375.

Edible Supramolecular Chiral Nanostructures by Self-Assembly of an Amphiphilic Phytosterol Conjugate

A. Sánchez-Ferrer, J. Adamcik, R. Mezzenga

ETH Zürich, Zürich, Switzerland.

INTRODUCTION: Phytosterols are sterols extracted from plants, and have structures similar to that of cholesterol.[1] They have been proposed as a natural source for the reduction of both cholesterol in blood plasma as well as cholesterol low-density lipoprotein, and recommended as a dietary supplement.[2] Besides regular phytosterols, conjugated phytosterols are also present in plants as fatty acids, acylated glycosides or glycosides derivatives.[3]

In this work, we discuss for the first time the spontaneous self-assembly behaviour of a conjugated glucose-sitosterol (β -sitosterolin), synthesized in our laboratory, and analogue to that found in several natural products. We rely on small and wide angle X-ray scattering (SAXS, WAXS) and on atomic force microscopy (AFM) for the study of the complex architectures of the colloidal objects based on supramolecular β -sitosterolin self-assembly.[4]

RESULTS & DISCUSSION: When adding drop-wise water or $^1\text{PrOH}$ (poor solvents) into a DMSO (good solvent) solution of β -sitosterolin, cloudy dispersions were rapidly obtained. The SAXS pattern of these dispersions showed the presence of different types of aggregates (Figure 1). β -sitosterolin was also dispersed in pure $^1\text{PrOH}$ which was stable upon time, while once dispersed in pure water it precipitated.

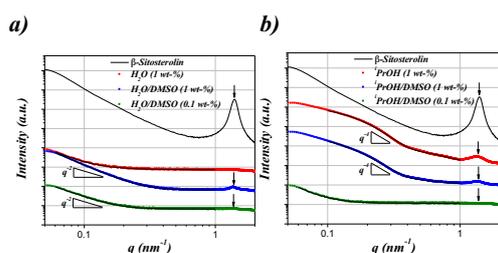


Fig. 1: SAXS pattern for dispersions of β -sitosterolin using a) H_2O , and b) $^1\text{PrOH}$.

All samples prepared by addition of $^1\text{PrOH}$ or water in DMSO show a scattering peak at around $q = 1.40 \text{ nm}^{-1}$ (arrow in Figure 1) which corresponds to the micro-phase separation length scale 4.5 nm already observed in solid state. Thus, micro-phase separation at this small length scale is maintained

also in solution, irrespective of the selective solvent considered.

AFM experiments showed different morphologies depending on the quality of the solvent used (Figure 2). Samples in $\text{H}_2\text{O}/\text{DMSO}$ (9:1) were confirmed to adopt a flat-like structure - glucose occupying the outer part of the flat side with multi-layer steps of 4.7 nm (Figure 2a). Some flat-like objects break down into highly elongated ribbons wrapping into helical ribbons of typical diameter of $24 \pm 5 \text{ nm}$ and pitch $90 \pm 10 \text{ nm}$ (Figure 2b). Samples in $^1\text{PrOH}$ showed objects of 4 to 5 nm in height and 40-50 nm in diameter (Figure 2c) - sitosterol exposed against the solvent in the outer part of the plates.

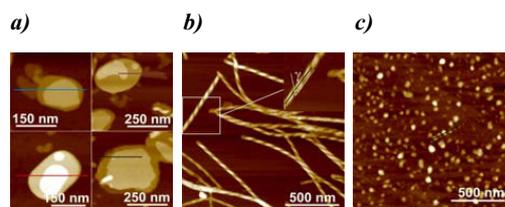


Fig. 2: AFM height images of the self-assembly of β -sitosterolin in $\text{H}_2\text{O}/\text{DMSO}$ showing a) platelet-like structures, and b) coexisting helical ribbons. AFM height images of the self-assembly of β -sitosterolin in $^1\text{PrOH}/\text{DMSO}$ (9:1) showing c) spherical aggregates.

CONCLUSIONS: The self-assembly of a phytosterol conjugate (β -sitosterolin) has been investigated in bulk, in molecular solution and in the presence of a selective solvent. Depending on the quality of the selective solvent, the molecule aggregates into molecular bilayers, in which the moieties facing the solvent can be either the glucose or the sitosterol units, depending on whether water (platelet-like structures and left-handed helical ribbons) or isopropanol (spherical-like object) are used as solvent, respectively.

REFERENCES: ¹ L.J. Goad; 1991; *Methods Plant Biochem*; 7:369-434. ² A. Ambring et al.; 2004; *Clin. Sci.*; 106:519-525. ³ M. Ohnishi et al.; 1981; *Phytochemistry*; 20:1357-1358. ⁴ A. Sánchez-Ferrer, J. Adamcik, R. Mezzenga; 2011; *Soft Matter*; accepted.

Liquid-Crystalline Elastomers in Microdevices

[A. Sánchez-Ferre^{b3}](#), [T. Fisch¹](#), [M. Stubenrauch¹](#),
[A. Albrecht²](#), [H. Wurm²](#), [M. Hoffmann²](#), [H. Finkelman³](#)

¹ ETH Zürich, Zürich, Switzerland. ² Technische Universität Ilmenau, Ilmenau, Germany.

³ Albert-Ludwigs-Universität, Freiburg, Germany.

INTRODUCTION: Microactuators are an essential component in technologies such as microsystems or microdevices, and in applications that include artificial muscles, pumps, valves or switchers.[1] The properties of these materials (actuation strain, reaction speed, density, driving voltage, consumed power), and the possibility of developing small dimension constructions with soft materials, are of high interest for industrial, medical and domestic uses.

Liquid-Crystalline Elastomers (LCEs) are a new class of actuator materials in the field of microsystem technologies, which can be used in standard processes. A rubber-elastic actuator is presented which provides new possibilities in microactuation due to its shrinkage when temperature increases. Such materials are suitable for the construction of microdevices (e.g. microgrippers and microvalves for microfluidics). The LCE actuator is a thermo-mechanical actuator, operated by electro-thermal power. We present two examples based on LCEs in microdevices. The first construction can be used for slow and precise positioning,[2] and the second for pumping mediums like liquids and gases.[3]

RESULTS & DISCUSSION: The first example on the integration of LCEs into microdevices is a model microactuator (Figure 1) which was constructed and thermally controlled. Its response was analyzed at different voltage rates, showing that the principle can be applied for technological applications: pumps, valves and switches. On applying an electrical power (voltage at different rates), the nematic-to-isotropic transformation induces changes of the liquid-crystalline elastomer film length that causes strains up to 150% in the microdevice and the capacity to move up to 400 times its own mass.

The second example is the successful integration of an oriented nematic side-chain LCE into a silicon-based microstructured device for the use as a microvalve for microfluidics. The new actuation principle is based on the expansion of the LCE in the directions perpendicular to the director and the shrinkage in the direction parallel to the director, all of which have been considered for the design of the device, based on the actuation of the LCE from the nematic to the isotropic state (Figure 2)

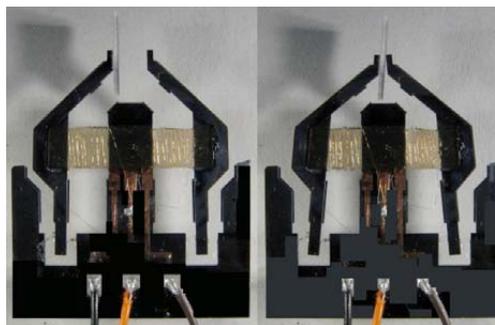


Fig. 1: Open (left) and closed (right) liquid-crystalline elastomeric microgripper.

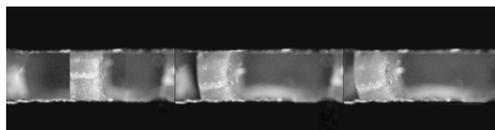


Fig. 2: Snapshot pictures during the actuation of the LCE microvalve. The actuator pushes itself at the end of the extension to the canal opening.

CONCLUSIONS : Liquid-crystalline elastomers (LCEs) are materials suitable for the application in Microsystems Technology, due to their good integration and their large strain values. A microactuator prototype has been developed and manufactured. Such an actuator is suitable for slow, sensitive positioning and gripping movements

A new microvalve, different from the existent commercial microvalves, has been design and constructed which controls the volumetric flow rate. Both microdevices are based on the main actuation principle for monodomains of a LCE (change in dimensions when passing from the nematic to the isotropic state).

REFERENCES: ¹ Y. Bar-Cohen; 2004; SPIE Press Monograph; Vol. PM136: "Electroactive Polymer Actuators as Artificial Muscles: Reality, Potential, and Challenges". ² A. Sánchez-Ferre et al.; 2009; Macromol. Chem. Phys; 210:1671-1677. ³ A. Sánchez-Ferre et al.; 2011; Adv. Mater.; 23:4526-4530.

Adsorption of polydisperse soft shell nanoparticles on liquid interfaces: A numerical study

Konrad Schwenke, Emanuela Del Gado

Microstructure and Rheology, Institute for Building Materials, ETH Zürich

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

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

It is elucidated how the characteristics of the adsorption process depend on the adsorption energy and the influx of particles and how the size distribution of adsorbed particles changes during this process [3].

References

- [1] L. Isa, E. Amstad, M. Textor, E. Reimhult, *Chimia*, 2010, 64, 145.
- [2] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press, 2002
- [3] L. Isa, E. Amstad, K. Schwenke, E. Del Gado, P. Ilg, M. Kröger and E. Reimhult, *Soft Matter*, 2011, 7, 7663-7675.

Fluid Characterization by Vibration Sensors Oscillating in Multiple Modes

[Thomas Wattering](#), [Tobias Brack](#), [Jürg Dual](#)

ETH Zürich, Zürich, Switzerland. Institut of Mechanical Systems/Center of Mechanics

INTRODUCTION: Vibration sensors are valuable tools in order to monitor fluid properties during industrial production processes as they allow quick and continuous measurements. Possible fields of applications are the food, chemical, petro-chemical or cosmetics industries, e.g. the mixing of beverages, the fabrication of inks for printers or the blending of fuels in refineries. While most vibration sensors described in the literature make use of a single oscillation mode^{1,2} the application of multiple oscillation modes is beneficial because of the different sensitivities of individual modes on fluid parameters. Two sensor concepts which employ multiple oscillation modes shall be presented here. The first one enables the combined measurement of density and viscosity of Newtonian fluids. The second one allows to investigate Non-Newtonian fluids at different frequencies.

MEASURING PRINCIPLE: In recent years a process viscometer has been developed at the Institute. This viscometer is based on a torsionally vibrating rod [Fig. 1], which is immersed in the sample fluid. With a Phase Locked Loop (PLL) the phase between excitation (e.g. excitation force) and response (e.g. velocity on sensor surface) can be held constant, by controlling the excitation frequency. This allows to capture the phase spectrum and resonance frequency of the oscillating system. The slope of the phase curve is related to the damping, which is composed of the structural damping of the rod and the internal friction forces in the fluid. This enables accurate relative viscosity measurements. Recently a digital version of a PLL has been developed, which provides multiple possibilities to extend the control procedure.



Fig. 1: Vibrating rod sensor

CONCEPT 1: Combined density and viscosity measurements of Newtonian Fluids. If absolute viscosity values are sought or if larger density changes are present, the density of the fluid must be provided to the sensor shown above.

A combined measurement of density and viscosity with the same sensor will render the sensor more versatile and enhance its accuracy. Therefore the

existing sensor shall be further developed to include density measurements. This can be achieved by exciting the rod to both flexural and torsional oscillations and evaluating damping and resonance frequency of these modes.

Experimental results with the three lowest bending modes in different fluids show an increasing sensitivity for higher order bending modes. A simplified analytical model provides first insights into the dependency of the bending resonance frequency on fluid density and viscosity.

CONCEPT 2: Characterization of Non-Newtonian Fluids. By operating the sensor at different frequencies, the measurement results in different damping values and resonance frequencies. As a viscoelastic fluid influences both the damping and resonance frequency, an iterative process leads to an identification of the fluid's properties and frequency dependence and thus to a description of the Non-Newtonian behavior.

The frequencies that can be used are restricted to the sensors resonance frequencies due to the working principle. As the digital PLL allows to freely design the control loop, it has been achieved to excite and control multiple frequencies consecutively as well as simultaneously.

DISCUSSION & CONCLUSIONS: The combination of information from multiple oscillation modes allows a more comprehensive measurement of fluid properties. By exploiting the different sensitivities of individual modes, higher measurement accuracy can be achieved. Frequency dependent measurements can be related to Non-Newtonian fluid behavior.

REFERENCES:

- ¹ da Mata, J., Fareleira J., et al;2001; High Temperatures - High Pressures;33(6): 723-727
- ² Krall, A. H. and Sengers J. 2003; International Journal of Thermophysics 24(2): 337-359
- ³ Ghatkesar, M. K., et al;2008; Sensors and Actuators B - Chemical 135(1): 133-138
- ⁴ Dinser, S., Dual J., Häusler, K.2008; AIP Conf. Proc.; 1027: 1186-1188
- ⁵ Reinhart W. H., Häusler K., Schaller P., et al.; 1998; Clinical Hemorheology and Microcirculation; 18(1): 59-65