#### **Adolphe Merkle Institute**

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# Annual Report 2008 of the Adolphe Merkle Institute

March 2009

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#### Preface

"Large donation for the University of Fribourg", "University of Fribourg receives research institute thanks to a large donation", these and other headlines appeared on the front pages of most Swiss newspapers at the end of November 2007. They announced the establishment of a private foundation by the Fribourgeois entrepreneur Adolphe Merkle in order to strengthen research and teaching at the University of Fribourg. This private donation, with 100 million Swiss francs the most important ever in Switzerland for a Swiss University, subsequently enabled the creation of a new interdisciplinary institute, the Adolphe Merkle Institute (AMI). What has happened since?

On January 1, 2008 the Institute officially started its operation with the transfer of a core group of 8 scientists from the Physics Department that formed the first research group of AMI, the "Soft Nanoscience Group". In the mean time the institute has rapidly expanded. At the end of 2008, the new head count has reached a total of 25 collaborators. This considerable growth reflects the fact that a number of successful grant applications to national and European funding agencies as well as project negotiations with industry have already resulted in a substantial contribution to the overall running and personnel cost of the soft nano group. Overall these external funds already cover approximately 60-70% of the total soft nano group budget for 2008 and 2009, despite the economic crisis that has resulted in significantly more difficult general conditions for finding external sponsorship.

The planning for the future scientific orientation of AMI has been an important milestone for the new institute. An international scientific advisory board (SAB) of eminent scientists from different areas such as (soft) condensed matter chemistry and physics, materials science, life science and nanoscience and – technology has been created. The SAB fully endorsed the original plan of creating four research groups, where the group leaders will be financed through the foundation, but hired by the university in the position of a full professor. The research of the institute will initially concentrate on the area of pure and applied nanoscience, with a strong focus on how to make, study and apply nano-based and nano-structured materials and systems using a soft nanotechnology approach that is based on bottom-up principles, self-assembly and "fab-less nano" strategies. Based on the advice given by the Scientific Advisory Committee during its first meeting, a search for a polymer chemist with a strong background in materials science had been started in summer 2008. In the mean time, AMI has been able to proudly announce the appointment of Christoph Weder, the F. Alex Nason Professor in Polymer Chemistry at Case Western Reserve University in Cleveland (USA), as a full professor in polymer chemistry at AMI.

Another important milestone for the development of the institute has been the planning of the further development of the experimental infrastructure and the project of a new dedicated institute building. The project for a new institute building has successfully been launched last year. In 2011 AMI should be able to move into its final home, where it will find state of the art laboratories for up to 160 researchers. A temporary solution for the first two groups of the institute has also been found for the intermediate period. An entire floor of a research laboratory building of Ilford in Marly, only a few minutes away from the Faculty of Science campus, with approximately 1!700 m<sup>2</sup> total surface has been rented, and all AMI activities have been moved into the new location on February 1, 2009.

This annual report now provides a short summary of the scientific activities that have developed during the first year of AMI!s existence. It is clear that AMI is still in its infancy, but the first signs of life have been quite promising, and we hope that 2009 will bring a similar rate of development as 2008!

Rentof

P. Schurtenberger, Director

Marly, 26 March 2009

# Soft Nanoscience Group – Main Research Activities in 2008

The soft nanoscience group focuses on fundamental and applied soft matter research, and aims at understanding the formation processes, structure, and functional properties of nanostructured systems that play an important role in real life. This research is not only driven by scientific curiosity, but we constantly seek to utilize our profound understanding of the equilibrium and non-equilibrium properties of soft matter systems such as colloids, polymers and surfactants in order to explore new routes towards nanotechnology-based applications.

The interaction between colloidal particles, their ability to form either highly ordered or amorphous structures, is of fundamental importance for novel applications in areas such as photonics or composite materials. In combination with polymers, hybrid nanocomposites have been developed to combine the advantages of both classes of materials and widen their application range. Here we design functionalized nanoparticles that can be used to create adaptive polymer-colloid nanomaterials with tailored optical, magnetic and mechanical properties. We investigate nanotechnology applications in areas such as life and food sciences.

Our scientific activities are centered on the following topics:

- Colloids as model atoms: Fundamental condensed matter research using colloids as versatile model systems
- Proteins as model colloids: How to use nanoscience to understand protein interactions and learn more about protein condensation diseases such as cataract formation
- Nanoscience and food: Bridging the gap from fundamental nanoscience and -technology to the formation of complex food systems
- Making and exploring novel materials: From responsive nanoparticles and polymers to intelligent materials with novel properties



# **Fundamental Colloid Research**



### Interactions in suspensions of iron oxide nanocubes by small-angle X-ray scattering

#### László ALMÁSY, Vikash MALIK, Hervé DIETSCH, Urs GASSER and Peter SCHURTENBERGER

Hematite nanocrystals are grown from coprecipitation of ferrous salts in aqueous solutions at a defined concentration. Varying the preparation conditions (salt concentration, pH, and amount of additives), quite monodisperse crystallites of cubic shape and of controlled size can be produced. Such particles are attractive for novel applications, for example, preparation of nanostructured surfaces of regular, in this case square array geometry. The dispersions themselves are also interesting due to their constituent particles, extremely uniform in size and shape. This project aims to describe the behavior of this colloidal system and its response to external conditions.



We study the suspensions of these cubic, canted antiferromagnetic or weakly ferromagnetic particles



in an external magnetic field by small-angle neutron and X-ray scattering, which give information on the size and shape of the constituting particles and their interactions at various conditions. In the first step, dilute dispersions of hematite nanocubes of 80 nm edge length have been measured by small-angle X-ray scattering on the cSAXS beamline of the SLS, under the influence of a magnetic field directed perpendicular to the incident photon beam. In zero field, the scattering pattern corresponds to the theoretical form-factor of an ideal cube (upper graph), showing that the particles are well dispersed and no interparticle interference is occurring.





in the direction of the field the oscillations of the single particle form factor are greatly reduced, which can be attributed to the correlation between neighboring particles along the field direction. In next experiments these interactions in a broad concentration range will be analyzed, and appropriate models will be developed.

Related investigations are planned for superparamagnetic nanoparticles encapsulated in a nonmagnetic shell, for example in a silica matrix. In this way, the strength of the magnetic interactions can be regulated which allows us to control the behavior of the colloidal system.

#### Hematite as model colloidal particles

#### Hervé DIETSCH, Vikash MALIK, Mathias REUFER and Peter SCHURTENBERGER

#### In collaboration with the Department of Physics, Fribourg, Switzerland (Camille DAGALLIER and Frank SCHEFFOLD)

Iron oxide hematite particles are ideal model colloidal particles. Varying the nature of the precursor, its concentration and the ionic strength of the medium allows us to fully control the morphology in terms of size, shape and aspect ratio of the obtained particles. Moreover, due to their magnetic properties, hematite can be oriented or locally concentrated applying a homogeneous or inhomogeneous external



These particles lose their magnetic properties but gain new interesting optical properties as one can easily match their index of refraction with that of the medium.

The thus-obtained particles can then be integrated in diverse matrices such as polymer nanocomposites (PhD thesis of Olivier Pravaz), used for magnetic fishing (collaboration with L. H. Liu and M. Yan Portland OR, USA), used to control the motion of microtubules on magnetic films (collaboration with Empa Dübendorf P. Stickar, M. Marioni, ETHZ Zürich V. Voegel) or more fundamentally to understand the anisotropic defect by

magnetic field.

To integrate hematite into a polymer matrix or to control their stability in any desired liquid medium, we systematically coated silica via a controlled pathway allowing for a surface modification using silane-coupling agents.

The figure on the left summarizes the ranges in terms of size, aspect ratio and surface functionality, which were obtained with these hematite systems. The figure is adapted from ref. [1]. Hematite can also be used as a nanotemplate leading to hollow silica shells with a desired shape depending on the hematite core used. On the electron micrograph bellow hollow spindle silica shells are presented.



integrating them into liquid crystals (collaboration with C. Blanc and M. Nobili, LCVN Montpellier, France). Their characterization in terms of size, shell thickness and porosity has required different means such as X-ray scattering under magnetic field, electron microscopy, surface area determination (BET) and more classical techniques such as IR and NMR.

[1] H. Dietsch, V. Malik, M. Reufer, C. Dagallier, A. Shalkevich, M. Saric, T. Gibaud, F. Cardinaux, F. Scheffold, A. Stradner, and P. Schurtenberger, Chimia 62, 805 (2008).

# Synthesis and characterization of novel functional electrosterically stabilized colloidal particles prepared by emulsion polymerization using a strongly ionized amphiphilic diblock copolymer

# Priti MOHANTY, Hervé DIETSCH, Laurent RUBATAT, Anna STRADNER and Peter SCHURTENBERGER

In collaboration with the Department of Polymer Chemistry, Kyoto University, Kyoto 615-8510, Japan (K. MATSUMOTO) and the Molecular Engineering Institute, Kinki University, 11-6 Kayanomori Iizuka Fukuoka Prefecture 820-8555, Japan (H. MATSUOKA)



Dispersion and emulsion polymerization are two well-known techniques to synthesize the so- called "latex" particles. The most used and synthesized latex particles are based on the polymerization of styrene. There are numbers of physical and chemical parameters which control the final size and monodispersity of the obtained particles, one of them is the use of an amphiphilic molecule in the synthetic milieu, which generally leads to smaller particles. In this work, we replace the classical "small" surfactant molecule by a much larger amphiphilic diblock copolymer poly(styrene)-block-poly(styrene sulfonate) (PS-b-PSS). PS-PSS polymers belong to a class of new polymeric surfactants, which strongly ionize in aqueous media. We investigated their selfassembly behaviour in aqueous solution and used them as an emulsifier to prepare electrosterically stabilized colloidal particles of different diameters between 70 to 400 nm. We determined the size, size polydispersity, effective charges, total dissociable charges,

their structural ordering and phase behaviour using light scattering, transmission electron microscopy (TEM), small angle neutron scattering (SANS) and potentiometric titration. These experiments clearly demonstrated that all the synthesized particles were almost monodisperse (polydispersity index ! 6



%).

The form factors obtained by SANS were well described by a polydisperse sphere model.

The data obtained fit perfectly the model as represented on the figure on the left. At very low ionic strength these

monodisperse particles were found to selfassemble into three dimensional ordered colloidal crystalline arrays at a low volume fraction of 0.00074 that diffract light in the visible region exhibiting properties of artificial opals (see photo on the right).



This work has been recently published in Langmuir [1].

[1] P.S. Mohanty, H. Dietsch, L. Rubatat, A. Stradner, K. Matsumoto, H. Matsuoka and P. Schurtenberger, Langmuir 25, 1940 (2009).

# Evanescent wave dynamic light scattering (EWDLS) of colloidal particles at liquid-liquid and solid-liquid interfaces

Tahereh MOKHTARI and Reinhard SIGEL

In collaboration with Forschungszentrum Jülich in Germany (Peter LANG and Jan DHONT) and FO.R.T.H-IESL in Greece (Benoit LOPPINET)

The objective of this work is to understand the diffusion dynamics of colloidal rod-like particles at liquid-liquid and solid-liquid interfaces.



The evanescent wave dynamic light scattering technique is a very powerful and useful tool for investigation of colloidal particles and polymers near the surface and interfaces without the influence of the particles in the bulk. In EWDLS–experiments, an evanescent wave is created upon total reflection of a laser beam at the interface between a liquid-liquid or solid-liquid interface. This evanescent wave is then used as the incident radiation for a dynamic light scattering experiment. Our setup (shown on the left) combines evanescent wave dynamic light scattering (EWDLS) with ellipsometry. Further, its flexibility allows for a three dimensional access of the detector to the scattering volume.

In our first experiment, polystyrene colloidal particles (52.3 nm) were dispersed at the dodecane-water interface. Prior to EWDLS measurements, the critical angle was determined via ellipsometry



technique. This technique will also verify if the polystyrene particles are dispersed at the interface or in the bulk solution. In the following figure, the ellipsometric quantities tan(!) and are plotted versus the reflection angle when the polystyrene particles were dispersed at the interface (solid symbols) compared to the bare interface (hollow symbols). In this figure, it can be seen that the addition of polystyrene particles at the interface has resulted in a shift in the Brewster angle, a shallower minimum of tan(!), and a related decrease in the slope of . Therefore, these measurements show that the

particles are dispersed at the interface. The surface concentration and the location of the particles at the interface can also be determined from these measurements. The EWDLS was then performed for this sample of which an example is shown below.



Our next goal is to investigate the translational and rotational diffusion of gold nano-rods at liquid-liquid and solid-liquid interfaces. We will then compare the dynamics of the rods for these two conditions.

#### Scattering on anisotropic magnetic particles

# Mathias REUFER, Camille DAGALLIER, Hervé DIETSCH, Urs GASSER and Peter SCHURTENBERGER

Magnetic colloidal particles are a class of materials widely used in many fields of colloid and materials science. The characterization of such particles is thus of great importance. Magnetic properties of individual particles are mostly measured on dried powders, where the individual particles are randomly oriented, and then re-scaled on the single particle. For anisotropic particles this approach gives only over all particle orientations averaged values. Scattering experiments allow in-situ measurements on the dispersed particles and for anisotropic particles the obtained 2D-scattering patterns can be directly linked to the orientation of the dispersed particles. By using an appropriate model the magnetic properties of the individual particles can be revealed.



The left figure shows scattering curves of diluted suspensions of hematite-silica core-shell particles with varying silica coating thickness. The lines represent fits using a prolate ellipsoid core-shell model. To further test the model we can fit the silica shell of the hollow particles, which can be obtained by etching away the hematite core with HCI (see right figure).



Finally we apply a magnetic field and integrate the obtained anisotropic scattering pattern parallel and perpendicular to the magnetic field direction (left image). By fitting the so-obtained scattering curves with a model incorporating the magnetic interaction energy of the hematite particles we are able to reveal the order parameter  $P_2$ , which stands for the mean orientation of the individual particles relative to the magnetic field. The so-found corresponding magnetic moment of the individual particles is in agreement with measurements on dried particles.

#### Glass transition studies on microgel systems

#### Mathias REUFER, Pedro DIAZ-LEYVA and Frank SCHEFFOLD

The possibility to tune the interaction between colloidal particles allows controlling bulk material properties, such as elastic modulus and viscosity, as well as optical properties. To achieve such behaviour thermo-sensitive microgels have been widely used. These materials have also received attention due to their potential applications in drug delivery or as sensors. Many previously investigated thermo-sensitive systems are based on poly(N-Isopropyl-Acrylamide) (PNIPAM), a polymer which has a lower critical solution temperature (LCST) of approximately 33°C. Below the LCST, water is a good solvent for PNIPAM, and PNIPAM microgel particles are swollen, while above the LCST, the microgel particles expel water and are partially collapsed. Thus, colloidal systems based on cross-linked PNIPAM microgel particles have tunable size and softness. We study these systems with traditional light scattering, Diffusing Wave Spectroscopy (DWS) and

We study these systems with traditional light scattering, Diffusing Wave Spectroscopy (DWS) and confocal microscopy [1]. The tunable interaction potential provides external control of the microstructural and viscoelastic properties. We report on the first full microrheological analysis of the viscoelastic properties of microgel particles undergoing a liquid to solid transition.



The left figure shows the temperature dependence of the PNIPAM particle size from static and dynamic light scattering. The lines are fits to the data using the core-shell model shown in the inset. In the figure on the right the dynamics measured by DWS on a highly concentrated sample is summarized. Above approximate 28°C the sample shows a liquid behaviour and the normalized diffusion time !/!<sub>0</sub> can be fitted with a hard sphere model proposed by Lionberger and Russel. Below this so-defined glass transition temperature of approximate 28°C we measure the onset of a plateau in the intensity correlation function (ICF) that can be converted into a shear modulus.

[1] M. Reufer, P. Diaz-Leyva, I. Lynch and F. Scheffold, European Physical Journal E : Soft Matter 28, 165–171 (2009).

# Charged ellipsoidal colloidal particles as model system with tuneable orientation and interaction



#### Chantal RUFIER, Hervé DIETSCH and Peter SCHURTENBERGER

Colloidal nanoparticles are increasingly important in biomedicine and various other applications. However, in order to integrate them into systems and to guarantee their stability, there is a need to understand and control their interactions in the respective medium. The overall goal of the project is to synthesize model particles with tunable attractive and repulsive interactions.

The core-shell model system structure we aim at consists of a magnetic core and a charged shell. Thus the attractive and repulsive interactions between particles of such a design can easily be tuned by applying an external magnetic field or field gradient, ionic strength or pH.

We developed new model particles by surface modification of ellipsoidal hematites. The iron core gives a magnetic moment, which allows controlling the orientation of ellipsoidal particles by applying a

magnetic field and their local concentration. However, this magnetic moment induces an attraction between particles, which can result in an irreversible aggregation. To avoid the particle aggregation, the repulsive interactions have to increase. In order to amplify the electrostatic repulsion and to add a steric repulsion, a negative polyelectrolyte (poly acrylic acid, PAA) is added onto the surface during a silica coating of hematites. By a one step synthesis the macromolecule is jammed into the silica shell. The picture from transmission electron microscopy (TEM) shows the thin silica layer on the hematite while the polyelectrolyte is not visible. The bands between 1800 and 1300 cm<sup>-1</sup> in the Infra Red spectrum prove the presence of PAA.



During the next year, the modified particle behaviour will be studied. We will determine the pH influence on the negative charge density using the zeta-potential. The PAA should increase the charged density and thus should induce a larger repulsion barrier that changes the particle organization in suspension. We will study this particle organization as a function of the concentration by small-angle X-ray scattering (SAXS).

Moreover, we aim to use this surface modification by coating as a general method, which would for example also help for the stabilization of diverse particles with optional size, shape and functionality. For example we might be able to modify superparamagnetic magnetite already synthesized during 2008 within our research group.

# Physics of the colloid shell, investigated by ellipsometric light scattering

#### **Reinhard SIGEL**

#### In collaboration with

Max Planck Institut für Eisenforschung, Düsseldorf, Germany (Andreas ERBE) and Max Planck Institute of Colloids and Interfaces, Golm, Germany (Klaus TAUER)

For the stabilization of colloidal systems against precipitation, the interface of the particles to the surrounding liquid plays an essential role. To prevent particle aggregation, the interface is covered either bv electric charges (electrostatic stabilization) and/or by polymer coils (steric stabilization). А recently developed experimental tool to access this interface is ellipsometric light scattering (ELS). Similar to classical reflection ellipsometry for the investigation of layers on a planar interface,



ELS detects interfacial layers on the spherical colloidal interface.

An important issue in practical applications is the size distribution in the colloidal sample (polydispersity). The effect of polydispersity on ELS measurements has been clarified theoretically [1] and experimentally [2]. ELS yields two parameters ( $\tan \Psi_Q$  and  $\Delta$ ) which represent the average particle (coherent part), and a third parameter ( $\tan \Psi_I$ ) which is additionally affected by the deviations of individual particles from the average and the profile of the illuminating laser beam (incoherent part). Understanding the effect of polydispersity is essential for interface investigations of colloidal particles. In addition, it is a first step to apply ELS on more complicated particle morphologies.

Further, a radial symmetric birefringence of polystyrene colloids was detected. Based on the stressoptical coefficient of polystyrene, the magnitude of the birefringence can be rationalized as an effect of the interface tension  $\gamma$  during the colloid synthesis, if the depth on which  $\gamma$  affects the polymer configuration is comparable to the extension of an entanglement in a polymer melt [2]. The result illustrates the close connection between colloid and interface science, and how this connection is accessed by ELS.

- [1] R. Sigel, A. Erbe, Applied Optics 47, 2161-2170 (2008).
- [2] A. Erbe, K. Tauer, R. Sigel, Langmuir (accepted).

# Phase behavior of mixtures of ferrofluids and non-magnetic colloids

#### Verena STÄDELE, Mathias REUFER, Hervé DIETSCH and Urs GASSER

#### A collaboration of the Adolphe Merkle Institute and Paul Scherrer Institut, Villigen, Switzerland

The fabrication of tailored structures on the nano- and micrometer scale is one of the hot topics in soft condensed matter research using colloids, nano- or micrometer sized particles suspended in a solvent. Good control of such suspensions can be achieved, because the interactions between colloidal particles in suspension can be tailored to some extent. Liquids, crystals, gels, and glasses are commonly observed and, in many cases, phase transitions from one state to another can be induced at will by changing an easily accessible parameter such as the salt concentration of the solvent.

Suspensions of ferro- or paramagnetic colloidal particles -- ferrofluids -- show interesting rheological properties that can be tuned with an external magnetic field. However, ferrofluids are also of great interest due to the structural ordering of the magnetic particles that is induced by a magnetic field.



Evidence of needle-like, columnar, lamellar, and pseudo-crystalline structures have been found. Therefore, the question arises whether ferrofluids can be used for the manipulation of nonmagnetic (diamagnetic) particles to induce structural order among non-magnetic particles. The exploration of the interplay between nonmagnetic and magnetic colloids and their phase behavior is the goal of this project. Generally, it is found that the onset of structural ordering among non-magnetic particles is facilitated in a mixture of magnetic and non-magnetic colloids in a magnetic field. In some cases it could be shown that this effect is not due to magnetostatic interactions but due to correlations between paramagnetic and non-magnetic particles. A major obstacle in the exploration of the structures and phase transitions in such mixtures is the strong absorption of visible light of ferrofluids. In many cases this makes microscopy and light

scattering studies impossible; both techniques are important tools in colloidal physics. Experimental techniques that are applicable to opaque samples are needed for ferrofluids; Small-angle neutron- and X-ray scattering are among the most important and are both available at the Paul Scherrer Institute.

In order to obtain a detailed understanding of the formation of ordered structures under an applied magnetic field, it is important to study particles with well-characterized structural and magnetic properties and with well-understood interaction in the absence of a magnetic field. For this purpose, spindle-shaped magnetic particles containing  $Fe_2O_3$  as hematite or maghemite have been produced and coated with silica shells of adjustable thickness. The magnetic core of such particles can be removed by etching and, therefore, non-magnetic particles with the same external properties of the silica shell can be obtained. As a consequence, mixtures of magnetic and non-magnetic particles with otherwise identical properties and interactions in absence of a magnetic field can be obtained. Preliminary measurements of the structural properties and the behavior under a magnetic field have been performed at SLS, Paul Scherrer Institute with samples containing purely magnetic or non-magnetic particles.

#### Liquid-solid transition in pH responsive microgels

#### Kitty VAN GRUIJTHUIJSEN and Hervé DIETSCH

#### In collaboration with RWTH-Aachen University, Germany (Priti MOHANTY)

In order to map the complete phase diagram of spheres, it is convenient to be able to tune the size and interactions with minor changes like temperature or pH. In this context poly(N-isopropyl acrylamide) (PNIPAM) microgel particles, which are temperature responsive, have been thoroughly investigated. Since these microgels are soft spheres in nature, extensions have been made to coated layers of PNIPAM on hard spheres. Depending on temperature this system will respond either like a hard or soft sphere. Another variation is the addition of charges to the microgel particles, via random copolymerization with a charged monomer. In this project we study the behavior of PNIPAM/poly(acrylic acid) (PAA) microgels at room temperature, as a function of pH with light scattering (SLS with 3D-cross correlation) and confocal laser scanning microscopy (CLSM).

A concentration series of 500 nm PNIPAM/PAA particles was measured with SLS at room temperature and neutral pH. The scattering data on the right clearly show a structure factor peak, which becomes more pronounced and moves to larger q values (indicating smaller particle-particle distances) with increasing concentration. We could also show that the position of the peak does not change with temperature, indicating the predominant influence of repulsions on the structure factor.





Larger PNIPAM/PAA particles of 1.2  $\mu$ m were non-covalently dyed with rhodamine and studied with CLSM at 1 wt% and room temperature. At low pH (upper image) the particles move freely, except from some clusters (circled). At higher pH (lower image), above the pl of PAA (4.2), particle movement is frozen, and a high structural ordering appears. The clusters at low pH seem to form large 'super-particles' (circled). This effect has been observed before, but is still not fully understood.

With particle tracking software the particle coordinates were determined in large data stacks. From the coordinates the pair distribution function g(r) was determined, as is shown below. These data confirm the sharp transition from particles with a steric soft-sphere repulsion at low pH, to particles with an electrostatic long-range repulsion at high pH.



#### Depletion interactions in aqueous model colloid-polymer mixtures

#### Kitty VAN GRUIJTHUIJSEN, Esther GROENEVELD, Hervé DIETSCH and Anna STRADNER

The investigation of non-equilibrium phenomena such as gel and glass formation in colloidal suspensions has emerged as one of the most important fields of soft matter research. Especially the interplay between short-range attraction and long-range repulsion, and its effect on the liquid –



disordered solid transition is still debated within the experimental and theoretical soft matter community. Numerous intriguing problems remain, and novel model systems are needed in order to shed light on the interplay between particle interactions and the resulting structural and dynamic state diagrams. Thus far, research on attractive depletion interactions has mainly been focussed on natural systems, with the added complexity of polydispersity and uncontrolled charges, and on model systems in organic solvents. This project

aims to fill the gap between model and natural systems, by investigating a model system in water consisting of polystyrene (PS) particles, either sterically stabilized by poly(ethylene oxide) (PEO) chains or electrosterically stabilized by a charged polymer, and PEO polymer. Our main interest focuses on the combination of tunable, charged particles with neutral PEO chains. However, since there is no encompassing, consistent study reported on these interactions with neutral, purely sterically stabilized particles in water, we choose to work on a neutral reference system first.

In order to be fully flexible in applying both direct space (confocal laser scanning microscopy (CLSM)) and indirect space (light, x-ray, neutron scattering) measurements, we decided to synthesize PS particles with a size of 300-600 nm. For most applications, latex particles are synthesized via emulsion or dispersion polymerization using ionic or non-ionic surfactants as non-covalent stabilizers. Since we will have to work at high volume fractions, a covalent stabilization is preferred, which can be achieved by (a) using PS-PEO diblock-copolymers as stabilizers, where the PS chain is anchored to the particle surface, or (b) using so-called macromonomers as stabilizers, which have a functional group that is co-polymerized with the PS.

Based on previous experience within our group, the first approach that we studied was stabilization of the PS particles with PS-PEO diblock-copolymer. Results from DLS and TEM looked invariably promising. However, the particles synthesized with an anionic initiator showed aggregation upon addition of salt and after concentration steps, indicating the lack of steric stabilization. The absence of

PS-PEO molecules on the PS particle surface was attributed to the frozen state of the PS-PEO micelles. The use of a non-charged initiator, which prevents the stabilization of secondary nuclei, indeed resulted in extremely low yields (< 5%) and large amounts of coagulum. Therefore, it was concluded that, following our procedure, PS-PEO diblock-copolymer plays a minor role in particle stabilization. The second approach, using macromonomers, is well known to yield monodisperse particles up to 150 nm. Currently we are attempting to increase the size, using new macromonomers, and a two-step synthesis procedure, known as seeded growth. An image of the first outcomes is shown on the right.



# **Biological Physics, Life and Food Science**







# Carbohydrate-decorated hematite nanoparticles for detection and decontamination of pathogens and toxins

#### Hervé DIETSCH and Peter SCHURTENBERGER

In collaboration with the Department of Chemistry, Portland State University (Li-Hong LIU and Mingdi YAN)



The detection and decontamination of biological threats are of prime importance in diagnostics, environmental monitoring, food safety control and homeland security. Carbohydrates have the unique ability to specifically interact with receptors on pathogen and toxins. Compared to proteins and enzymes that are often fragile and unstable, carbohydrates are stable entities. They are inherently biocompatible, non-toxic, and non-immunogenic.

The group of M. Yan is specialized in photochemically reactive surface modifications. We combine our knowledge to create a simple and versatile photochemically reactive hematite colloidal particle, which has been modified with a homemade phosphate agent: PFPA-P04, which adsorbs onto surface of the hematite. The next step was then the immobilization of D-mannose on hematite leading to particles able to decontaminate pathogens and toxins. As a proof that this nanomaterial is working, they were bound with *Con A*, a mannose-binding protein, which due to its multifunctionality leads to aggregation of the hematite as presented on the electron micrograph [1].



PFPA-hematite nanoparticles Mannose-hematite nanoparticles

Con A bound to Mannosehematite nanoparticles

An important example for a potential application of these surface modified hematite particles is magnetic fishing of selected bacteria.

[1] L. H. Liu, H. Dietsch, P. Schurtenberger and M. Yan, paper in preparation

#### Interactions between poylphenols and proline rich proteins

#### Graeme GILLIES and Anna STRADNER

#### Research into astringency at the Adolphe Merkle Institute started in October 2007 as a part of the ongoing collaboration between Nestlé and the University of Fribourg

The sensation of astringency is thought to arise from the interaction between polyphenolic compounds (tannins) and salivary proteins. Polyphenols are known to show a strong binding behaviour with proline amino acid units, a major subsistent of saliva proteins. The binding of tannins to protein molecules changes the protein from an open structure to a globule like conformation. The conformational change helps to solubilise the tannin but drastically changes the properties of the protein. In terms of sensations felt within the mouth, once saliva proteins take on a globule structure they loose their lubricating ability resulting in a sensation of dryness. A survey of proteins reveals that it is only proteins rich in proline that are able to bind with astringent molecules, and this functionality is unique to proline amino acids.

A comparison of poly-I-proline (PLP), poly-vinylpirrolidone (PVP), proline rich proteins (PRP), and polyaminomethylpyrrolidonesuccinimide (PAMPS) revealed that it is the 5 membered ring on the polymer backbone which governs the astringency interaction. All of the afore mentioned polymers bind astringent molecules via hydrophobic association. For polymers such as PVP, which have a 5 membered ring as a pendant chain this hydrophobic association is weak and somewhat reversible. However, placing the same 5 membered ring within the backbone, e.g. PAMPS, results in an additional conformational restriction and increases the free energy of the unit. Such polymers bind astringent molecules strongly, and the association cannot be reversed, since the entropic penalty of separating the two molecules is too high. The binding of astringent molecules to PAMPS, and the induced conformational changes and aggregation corresponded exactly with what is observed with PLP and PRPs. Such coincidences suggest that it is proline's 5 membered ring that controls the astringency sensation.



The project gives us another tool for designing small architectures and has lead to a further collaboration with Nestlé.

#### Interplay between phase-separation and gelation in protein – biopolymer mixtures



#### Najet MAHMOUDI and Anna STRADNER

Mixtures of polysaccharides and proteins have been shown to aggregate and phase-separate by thermodynamic incompatibility. complex coacervation, or through depletion interactions [1]. A proper understanding and control of different interactions between proteins and polysaccharides should thus enable food scientists to develop new food products with desirable structural properties. Analogies between model systems in colloid physics and much more complex food systems have started to be utilized to advance our knowledge of colloidal food systems [2, 3]. Important recent developments in soft matter research are linked to interparticle

interactions and stability of self-assembled particles, phase separation, and the phenomenon of dynamical arrest, i.e. the formation of gels and glasses [4]. The competition between spinodal decomposition and dynamical arrest and the possibility to modify this interplay by tuning the interparticle interaction strength and range holds a high potential both from fundamental soft matter physics as well as from an applied food science point of view. Moreover, it opens routes to achieve gels at intermediate concentration range only by mixing two components without the necessity of for example heat treatment or pH variation. The goal of the project is to study the structural and dynamical properties of casein micelles – biopolymer mixtures with a special emphasis on gel-like structures, using a combination of rheology, diffusing wave spectroscopy (DWS) and confocal laser scanning microscopy (CLSM).

In mixtures of high molecular weight xanthan and skim milk powder (SMP), a macroscopically arrested phase separation was observed at high xanthan concentrations. However, the formation of these gellike structures cannot be attributed to the formation of a continuous, structure-building network of the SMP rich phase since the xanthan forms a highly viscoelastic structure at the probed concentrations, whose characteristics are in the same order of magnitude as those of the compacted casein phase. In order to follow the original idea of this project, which is the instrumentalisation of an arrested spinodal decomposition process in order to create gels with well-defined structural and mechanical properties via polymer-induced depletion attractions, we replaced the relatively high molecular weight xanthan with a low molecular weight polymer displaying a much higher overlap concentration. In a first step we started to look at aqueous mixtures of casein micelle powder - a product which contains a considerably smaller amount of secondary components compared to skim milk powder - with the synthetic polymer polyethylene oxide (PEO), where preliminary results support the formation of a space-spanning casein network at higher PEO concentrations. As a next step, besides detailed rheological and DWS investigations of the arrested samples, a systematic light scattering study to determine the second virial coefficient of casein micelles as a function of added PEO is planned. This will lead to a generalized casein micelles - PEO phase diagram which allows comparison with other systems where the predominance of a tunable short-range attraction causes a rich phase behaviour.

- [1] J.-L. Doublier, C. Garnier, D. Renard, C. Sanchez, Current Opinion in Colloid & Interface Science 5, 202-214 (2000).
- [2] S. Bhat, R. Tuinier, P. Schurtenberger, Journal of Physics: Condensed Matter 18, L339–L346 (2006).
- [3] A. M. Donald, Nature Materials 3, 579-581 (2004).
- [4] F. Cardinaux, T. Gibaud, A. Stradner, P. Schurtenberger, Physical Review Letters 99, 118301 (2007).

#### Stability of Casein Micelles

#### Christian MOITZI, Peter SCHURTENBERGER and Anna STRADNER



Skim milk is a colloidal suspension of casein micelles, formed via self-assembly of four casein proteins and calcium phosphate, which are dispersed in an aqueous solution of salts, lactose and whey proteins. Different processes used in the production of milk gels rely on the destabilization of the casein micelles. In the production of cheese the stabilizing hairy layer on

their surface, which is providing the stability of the particles, is cut off by chymosin. In the yoghourt making process the pH of the milk is lowered by the action of lactobacilli, which convert lactose into lactic acid. Because of the shift in pH the hairy layer loses its charge and eventually collapses onto the surface of the micelle. Aggregation and gelation of particles in complex fluids represent prime examples where direct links between fundamental research and applications in food sciences can be made. Multi-angle static and dynamic light scattering has been shown to be an ideal method for determining the stability for systems where one can work in highly dilute and correspondingly singly scattering solutions. However, when it comes to industrially relevant systems one often has to deal with concentrations where multiple scattering becomes a problem.

To overcome this we are using a novel multi-angle light scattering instrument which implements the 3Dcross-correlation scheme and allows for timeresolved measurements in turbid suspensions. Detailed investigations on the sequence of internal aggregation structural rearrangements and phenomena that occur during skim milk acidification were done. The experiments provide us with convincing evidence that the structural rearrangements upon acidification are strongly dependent on the casein concentration. Therefore it is important to look at the process at its natural concentration, which is for milk in the regime of excessive multiple scattering.





The theoretical calculation of the casein interaction improved our understanding of the initial stages of the yogurt and cheese making processes. However, we found significant deviations of the stability determined experimentally from the theoretical prediction. These deviations have to be interpreted in analogy to the findings when model colloids were used. There a quantitative agreement of the experiment with the theory was only found at low ionic strength, which means at high separation distance of the repulsive barrier in the interaction potential. At high ionic strength the stability which was found in the experiments was much lower than predicted. The discrepancies are caused by additional

attractive effects which are not taken into account in the simplified model. These effects are for instance surface heterogeneities, the discrete nature of charges, and the finite size of ions and water molecules. The repulsive barrier in the interaction potential of casein micelles is at a separation distance smaller than 1nm. Therefore similar deviations from the theory are found.

Manuscript in preparation

#### Characterization of Heat Induced β-Lactoglobulin Microgels

#### Christian MOITZI and Anna STRADNER

In collaboration with the Nestlé Research Center (Laurence DONATO, Christophe SCHMITT)

 $\beta$ -lactoglobulin is the major whey protein of cow's milk (~3 g/l), and is also present in many other mammalian species; a notable exception being humans. Their main biological role is being a valuable food source, but supposedly it is also involved in the transport of hydrophobic molecules, which adsorb on it. Whey proteins are widely used in the food industry because of their high nutritional value. They are conferring interesting structural and textural features to food products. Heat treatment is commonly used in food industry for ensuring microbiological safety. It can greatly affect properties of whey proteins, which lose their native structure and unfold cooperatively and expose side-chain groups buried originally inside the molecular structure. Denaturation and aggregation depend on the balance between inter- and intra-molecular attractive and repulsive



forces, which are strongly affected by the conditions such as temperature, pH and ionic strength. For instance, heating of  $\beta$ -lactoglobulin solutions at low pH and low ionic strength leads to the formation of a transparent fine stranded gel which consists of long stiff fibres. At neutral pH a network of spherical aggregates is formed. In contrast to that a dispersion of stable spherical microgels of a relatively narrow size distribution was identified upon heating a demineralised solution to 70 and 85 °C at mild acidic pH (pH 5.7 - 5.9). Numerous applications require stable preparations of high protein concentration and low viscosity. The relatively dense microgel particles can be concentrated without leading to gelation. This makes them very interesting for the food industry.



A combination of small angle x-ray scattering and static and dynamic light scattering was used to characterize the native and heated samples in terms of their particle size, their aggregate mass, and their internal mass distribution. Along with the structural characterization of the product the main interest was to obtain information about the mechanism particle of the formation. The aggregation number of the unheated, native protein was found to be about 2 at neutral pH and about 1 at pH 2. This is in perfect agreement with literature values. If the pH of the solution is shifted from neutral towards the isoelectric point the mean aggregation number increases. A detailed analysis of the size

distribution shows that this is the result of the formation of a small number of soluble aggregates containing several protein molecules. The main fraction, however, stays dimeric. Upon heating microgels of about 200 nm in size are formed. Their aggregation number drastically increases with temperature. At the same time their size is changing only little which means that their density is increasing. If the microgels are removed by centrifugation one finds still some soluble aggregates present. After detailed analysis of the temperature dependence of the concentrations of native protein, soluble aggregates, and microgels we believe that the soluble aggregates represent an intermediate step in the formation of the microgels. This statement is supported by small angle x-ray scattering experiments which show that the microgels are internally structured on a length scale which corresponds to the size of the soluble aggregates.

Manuscript in preparation

#### Arrested phase separation in concentrated casein – xanthan mixtures

#### Kitty VAN GRUIJTHUIJSEN, Vishwa HERLE, Peter SCHURTENBERGER and Anna STRADNER

Many food products consist of mixtures of polysaccharides and proteins, which determine their structure, texture, and sensory properties. However, above certain polysaccharide concentrations these mixtures can phase separate into a polysaccharide-enriched and a protein-enriched phase. A thorough understanding of biopolymer interactions is essential to engineer tailored food materials. In order to quantify these interactions, this project focuses on a model system containing only two biopolymers, i.e. xanthan gum and casein micelles from skim milk. Previously, we established the coexistence curve of these mixtures, which was well described by depletion theory for mixtures of colloids and polymer chains in a background solvent, taking into account interactions between the polymer chains in the excluded volume limit [1].

The observation of an arrested phase separation at xanthan concentrations well above the coexistence curve, led to the speculation that – just as for mixtures with polymers that are smaller than the colloids – the casein-enriched phase forms a space-spanning network, which enforces the overall structure, preventing further phase separation. We studied the structural properties of casein and xanthan mixtures at high xanthan concentrations (1-7 g/L) using confocal laser scanning microscopy (CLSM), rheometry, and diffusing wave spectroscopy (DWS). The rheometry data of the mixtures are shown below, labeled according to the casein volume fraction. They clearly show that the addition of casein only increases the effective xanthan concentration in the continuous phase, neither enforcing, nor weakening the xanthan network. Moreover, rescaling the rheometry data onto

one master curve showed a dramatic increase of the relaxation time (data not shown) - measured as the cross-over of G' and G" with increasing xanthan concentration. Noticeably, there is no sharp increase around the concentration above which the samples macroscopically remain mixed over weeks (0.5 wt% xanthan). Therefore, the arrested phase separation is not an abrupt transition, but rather an effect of the guickly changing structural ordering of xanthan.



#### Cluster, glass, and crystal formation in concentrated protein solutions



#### Ilja VOETS

The phase behaviour of colloidal systems has been a subject of intense research for many decades. Recent advances include the discovery of equilibrium cluster phases, the existence of two different types of glassy states (attractive and repulsive), and ionic colloidal crystals of oppositely charged particles. Great efforts have been undertaken, both experimentally and theoretically, to map, describe, and explain the entire phase diagram, including equilibrium and non-equilibrium states. All are associated with a large set of intriguing dynamic and static properties, phase transitions, coexistence regions, and so forth.

The aim of this project is to investigate the phase behaviour of biocolloids, more specifically globular proteins, and to interpret the results in terms of colloids with an attractive short-range plus a repulsive hard core potential in combination with a long(er)-range moderate repulsive (electrostatic) potential. The experimental methods we use are scattering techniques (static light scattering, 3D dynamic light scattering, small-angle neutron and X-ray scattering), spectroscopy, differential scanning calorimetry, and rheology.

Concentrated lysozyme solutions were shown to exhibit unusual phase behaviour, including stable inhomogeneous phases, dynamically arrested states, and equilibrium cluster phases.



Succinylation of lysozyme (the reaction scheme is depicted above) yields so-called succinylated lysozyme having the same nominal charge, but opposite charge sign as compared to the parent protein. Presently, we focus on the optimization of the succinylation procedure and its effect on the physico-chemical and structural properties of lysozyme. Subsequently, we will investigate the phase diagram of this derivative, as well as the phase behaviour of mixtures of lysozyme and succinylated lysozyme.

This research project has been awarded two (personal) research grants: the Rubicon grant of the Dutch National Science Foundation and a Marie Curie Intra-European Fellowships within the Seventh Framework Programme of the European Commission.

# Towards understanding protein mixtures in the eye-lens

#### Malin ZACKRISSON, Anna STRADNER and Peter SCHURTENBERGER

#### In collaboration with the Rochester Institute of Technology, USA (George M. THURSTON) and EPFL and IRRMA, Lausanne (Nicolas DORSAZ, Giuseppe FOFFI)

The optical properties such as the index of refraction and transparency of the eye lens depend on the properties of concentrated solutions of proteins. In the lens, confined in highly ordered fibers, one finds the three main classes of proteins; alpha- ( $\alpha$ ), gamma- ( $\gamma$ B) and beta-crystallins ( $\beta$ ). They need to last a lifetime in the lens since there is no exchange after the lens is formed. When these proteins are unable to remain homogeneously distributed the lens becomes less transparent and ultimately the formation of cataract is unavoidable. In this project we investigate the interplay between these proteins



using powerful scattering techniques such as Small-Angle Neutron Scattering (SANS) and Dynamic and Static Light Scattering (DLS, SLS) where we can focus our attention rather on concentration effects, phase transitions and aggregation phenomena than on the traditional singleprotein molecular information. The goal of the project is thus to study the structural and dynamical properties of eye lens protein solutions, pure components as well as mixtures, and investigate their dominating interaction forces to understand aggregation behaviour and phase transitions.

Recently we could show by combining SANS measurements and computer simulations that between the  $\alpha$  and the  $\gamma$ B a delicate balance of attractive interactions manages to stabilize the protein mixture [1,2]. However, the role of the third protein,  $\beta$ , is relatively unknown. Despite its sequence similarity to  $\gamma$ B,  $\beta$  interact overall repulsively. In the next step we added this protein to the mixtures. Below is shown how the cloud points (T<sub>c</sub>) i.e. the temperature of phase separation is shifted when

 $\alpha$ 's or  $\beta$ 's are added to a solution of  $\gamma B$ 's at concentrations comparable to those found in the lens. Whereas the alphas initially destabilize the solution, the betas appear to have an overall stabilizing effect. Interpretation of the corresponding scattering requires a careful analysis, which is currently undertaken in collaboration with Prof. G. Foffi and co-workers at EPFL.



The phase diagram and the corresponding SANS measurements show the opposing effect of  $\beta$  and  $\alpha$  on the phase behavior of  $\gamma B$ .

A. Stradner, G. Foffi, N. Dorsaz, G.M. Thurston, P. Schurtenberger, PRL 99, 198103 (2007).
N. Dorsaz, G. Thurston, A. Stradner, P. Schurtenberger, G. Foffi, J. Phys. Chem. B (Web publication December 10, 2008)

# **Materials Science**



# Structure – properties relationship in proton conductive sulfonated polystyrene-polymethyl methacrylate block c opolymers (sPS-PMMA)

#### Hervé DIETSCH

# In collaboration with the Department of Physics, Polymer Physics Group, Fribourg, Switzerland. (L. RUBATAT, C. LI and R. MEZZENGA)

Within this collaboration we studied the dependence of proton conductivity on the morphologies of sulfonated polystyrene-poly(methyl methacrylate) (sPS-PMMA) diblock copolymers.



Our role in this project was to modify the polystyrene (PS) group of three different diblock copolymers of varying molecular weight and block volume fraction. We controlled the degree of sulfonation by changing the time of reaction and concentration of a non-commercially available chemical acetyl sulphate, which was freshly synthesized prior to the sulfonation. The degree of sulfonation was then checked using <sup>1</sup>H NMR of the considered PS blocks.

The investigation of the morphologies of the self-assembled sPS-PMMA diblocks was carried out in both dry samples and samples saturated with water using small-angle neutron scattering (SANS), transmission electron microscopy (TEM) and cryoTEM. Depending on molecular weight and sulfonation degrees, isotropic phases (ISO), lamellar phases (LAM), cylindrical hexagonal phases (HEX) and hexagonally perforated lamellae (HPL) were observed. The lamellar morphologies underwent marked volume expansion upon water pick up, while negligible swelling was detected for the other morphologies. The proton conductivity was measured in both the dry and wet states, the latter conditions resulting in an enhancement of conductivity of up to 3 orders of magnitude. In particular it was shown that the conductivity, normalized by the volume fraction of the conductive domains (formed by PS, sPS and water), rises monotonically with the content of sulfonic groups, and with the following sequence of morphologies: ISO - HEX - HPL - LAM, accompanied by discontinuities in correspondence of order-to-order and order-disorder transitions. The figure shows three cryo-TEM pictures of different samples exhibiting the following structures from top to bottom: lamellae, hexagonal and hexagonally perforated lamellae. This work was published in Macromolecules [1].

[1] L. Rubatat, C. Li, H. Dietsch, A. Nykänen, J. Ruokolainen and R. Mezzenga, Macromolecules 41, 8130-8137 (2008).

### Methods for functionalization of microsized polystyrene beads with titania nanoparticles for cathodic electrophoretic deposition

#### Hervé DIETSCH

#### In collaboration with EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Mechanics of Materials and Nanostructures, Thun, Switzerland (Simona RADICE and Johann MICHLER)

Assembling nanosized particles onto the surface of microsized particles in a defined way is challenging. This project is the PhD thesis of Simona Radice. We worked together on the assembly of TiO<sub>2</sub> nanoparticles (D=120nm) on the surface of monosized polystyrene beads of 4.6  $\mu$ m in diameter using combined polyelectrolytes and heterocoagulation with electrophoretic deposition (EPD). The aim of the project was to deposit titania–polystyrene (TiO<sub>2</sub>–PS) composite particles on Ti<sub>6</sub>Al<sub>4</sub>V substrates. A systematic study using zeta potential helped us to understand the relavant parameters to control the assembly of TiO<sub>2</sub> onto PS. We managed to optimize the conditions in terms of pH and concentration

(especially from the polyelectrolyte) and conclude that too less or too much do not give the desired results. On the right hand side, the zeta potential of PS particles is measured with different amounts of polyeletrolyte at a fixed pH, which increase due to the negative charges from the carboxyl groups on the PS surface.





Factor of theoretical full coverage of PDADMAC on PS beads

Two methods for the preparation of suspensions with  $TiO_2$ –PS composite particles in isopropanol were developed, where nanosized  $TiO_2$  particles covered the surface of microsized PS beads. The suspensions could then be used for cathodic EPD onto metallic substrates at EMPA, with all the related advantages of the EPD technique and the cathodic (rather than anodic) reaction at the substrate. The method based on the use of a polyelectrolyte optimized in Fribourg was found to be superior in terms of more complete adsorption of the TiO<sub>2</sub> particles onto the PS beads and led to a common publication [1]. The pictures on the left are scanning electron micrographs of  $TiO_2$  assembled onto the surface of PS microsized particles. Multiscale structured surfaces with the same system have also been prepared during this year [2].

[1] S. Radice, P. Kern, H. Dietsch, S. Mischler and J. Michler, Journal of Colloid and Interface Science 318, 264–270 (2008).

[2] S. Radice, H. Dietsch, J. Michler and S. Mischler, in preparation

### Controlling movement using magnetically patterned surfaces and magnetic tags

#### Hervé DIETSCH

# In collaboration with EMPA Dübendorf (Pablo STICKAR, Miguel MARIONI) and ETHZ (Viola VOEGEL)

Molecular motors can be used as nanoscale transport systems, which allow the controlled movement of selected cargo, driven from and to the desired place via a defined way. In reality, existing systems such as microtubule shuttles are known as systems which can move but without control of their direction.

In the present challenging work (PhD of Pablo Stickar), we collaborate to established magnetic beads which bind the microtubule surface. The thus obtained microtubules can then be moved onto a kinesin surface modified magnetic film. The magnetic film is basiccally defining the way and the weakly magnetic particles (canted antiferromagnetic hematite) can follow the way without sticking and inhibiting the microtubule to move.



The picture on the left represents the ideal system. We develop amino surface modified silica coated hematite particles in a first step, which could be further modified in order to bind biotin groups on the surface of the particles. We are currently working on the control of the number of functionalities to avoid aggregation of microtubules thanks to our multi functional biotin modified hematite.

#### Hematite and magnetite nanoparticles with tailored magnetic properties

#### Vikash MALIK, Peter SCHURTENBERGER and Hervé DIETSCH

# In collaboration with the Physics department, EPFL, Lausanne, Switzerland (Simon GRANVILLE and Jean-Philippe ANSERME)

Magnetic nanoparticles are increasingly important for their uses in biomedicines and various other applications. To obtain monodisperse particles, there is need to develop some controlled synthesis techniques so as to obtain colloids with tuneable size, shape, physical, magnetic and chemical properties. Particularly well-known and increasingly studied classes of particles are oxides. We have synthesized iron oxide nanoparticles (hematite and magnetite) of various size, shape and anisotropy, which exhibit different magnetic properties. The formation of hematite is a two-step process. In the first step akaganeite ( $\beta$ -FeOOH) is formed as an intermediate product before the final hematite nanoparticles form in the second step. The size of this intermediate product can be tuned by varying the iron salt concentration. The final hematite size and shape can be controlled with various parameters such as for example the pH of the solution, the salt concentration, the amount of additives and the temperature. The concentration of these intermediate products has been found a new parameter to control the size, shape and crystallinity of the hematite colloids.



TEM image of akaganeite nanoparticles



TEM image of Hematite nanocubes

The hematite nanoparticles obtained by adjusting the concentration of the intermediate products are single crystal in nature and exhibit different magnetic properties. Selected Area Electron Diffraction (SAED) and High Resolution Transmission Electron Microscopy (HRTEM) confirm the single crystalline nature of the existing nanocubes. Magnetic properties (coercivity and remnant magnetic moment) of these nanoparticles are directly proportional to their size i.e larger (140 nm) cubes show more coercivity and remnant magnetic moment than small nanocubes (60 nm). The temperature dependence of the magnetic moments has also been studied in order observe magnetic transitions from ferromagnetism to to antiferromagnetism (Morin transition). Large size nanocubes (140 and 180 nm) do not exhibit any transition over a range of temperature (340 K to 10 K). That may be due to the oxide and hydroxide ions present within the hematite crystal.

Together with hematite, we are also working on the synthesis of superparamagnetic nanoparticles. These colloids show a very high magnetic moment even in low external magnetic fields. The magnetic properties can be tuned by varying the silica shell thickness, the size of the magnetite core and the number of magnetite nanoparticles.



We characterized our homemade magnetic colloids with Transmission Electron Microscopy (TEM), X-Ray Diffractometry (XRD) and BET. The colloidal stability was investigated by measuring the zeta potential. The magnetic property measurements were carried out using a Magnetic Properties Measurement System (MPMS) at the Physics department at the EPF Lausanne. The results on hematite particles of different morphology have been published in a review article (1).

SAED and HRTEM of hematite nanocubes (90 nm)

[1] H. Dietsch, V. Malik, M. Reufer, C. Dagallier, A. Shalkevich, M. Saric, T. Gibaud, F. Cardinaux, F. Scheffold, A. Stradner, and P. Schurtenberger, Chimia 62, 805 (2008).

#### Synthesis and characterization of nanocomposites

Olivier PRAVAZ, Hervé DIETSCH and Peter SCHURTENBERGER

In collaboration with the European project named "Multi-Scale Modelling of Nanostructured Polymeric Materials: From Chemistry to Materials Performance" (BASF SE, Technische Universität Darmstadt, National Technical University of Athens, Friedrich-Alexander Universität Erlangen-Nürnberg, Gritche Technologies, Forschungszentrum Jülich GmbH, CULGI B.V., Centro Richerce Plast-Optica Spa, Universita degli studi di Trieste, Robert Bosch GmbH)



The goal of this project is to better understand nanocomposites, allow for a rational design of them, and overcome dispersion and stability problems. The approach is to develop, implement and validate multiscale methods to compute the mechanical, thermochemical and flow behavior of nano-filled polymeric materials – based on the chemistry of selected model systems. This project remains a challenge due to the very complex miscibility of inorganic particles with organic monomers. However, we successfully developed a "model synthesis" to disperse silica nanoparticles without aggregates in a PMMA (plexiglass) matrix based on previous work performed in this team and reported in [1]. We produce silica particles by the well-known Stöber synthesis [2] and cover them by a silane-coupling agent (typically TPM). This agent fixes the silica surface and contains an organic part that allows a full dispersion in a monomer. The particles in this colloidal suspension are called "Hybrid Monomers" as they can be

polymerized. In a next step we start the radical-free polymerization by adding an initiator under heating or UV-exposure. It is also possible to follow the in *situ* polymerization by light scattering or small-angle X-ray scattering (SAXS) as shown in the figure below.



We also have the possibility to cover the surface of different nanoparticles eith a silica shell of well-controlled thickness [3]. This access to different nanoparticles allows us to tune the mechanical, optical or magnetic properties of the resulting nanocomposites. We are currently working on the optimization of our model synthesis. In a next step we will study the effect of different critical parameters on the tuning properties of these composites. We will start with looking at the influence of the particle concentration, the material they consist of (iron oxide, latex, etc.), the particle size and shape (cube, ellipsoid, sphere, etc.).

- [1] M. Saric, H. Dietsch, P. Schurtenberger, Colloids and Surfaces A 291, 110-116 (2006).
- [2] W. Stöber, A. Fink, E. Bohn, Journal of Colloid and Interface Science 26, 62-69 (1968).
- [3] C. Graf, D. L. J. Vossen, A. Imhof, A. van Blaaderen, Langmuir 19, 6693-6700 (2003).

# **Other Areas**



#### Solution structure of dendronized polymers

#### Yen-Cheng LI, Reinhard SIGEL and Peter SCHURTENBERGER

In collaboration with ETH Zürich (Dieter SCHLÜTER and Afang ZHANG)

The effect of side chain architecture and electrostatic interactions on the flexibility of polyelectrolytes (PEL) has been the subject of intense experimental and theoretical investigations and yielded highly controversial results. The approach to PELs in solution is particularly challenging for theoreticians and experimentalists mainly due to two fundamental features of PELs: the long-range nature of the Coulomb interactions, and the influence not only of the solvent, as in the case of uncharged polymers, but also of counterions, and added salt ions. In recent years an interesting new class of polymers and polyelectrolytes has been developed, the so-called dendronized polymers. The goal of this on-going project is the experimental separation of steric and electrostatic stiffening effects using neutral and charged dendronized polymers.

Dendronized polymers (DP) are chain-like macromolecules with dendritic side groups. The bulky shape of these side groups restricts the conformation of the macromolecular backbone. As a





consequence, a stretched conformation of DP precipitated on a surface is reported in the literature. Surprisingly, in small angle neutron scattering (SANS) measurements for a characterization of the solution configuration of DP, no clear evidence for a stretched, rod-like molecular shape was found. A detailed evaluation of SANS data resolved this apparent contradiction: the expected rod asymptote in SANS data is hidden by effects caused from the finite molecular cross section.

Systematic SANS and SAXS experiments will provide us with quantitative information on the influence of the bulky side chains of dendronic polymers on the intrinsic chain flexibility, a topic of considerable interest in fundamental and applied polymer science. The comparison of data obtained with neutral and charged DPs will allow for a systematic investigation of the electrostatic interactions on chain flexibility and the degree of interchain correlation. The unique model system will allow for a quantitative test of the previously derived relations for the structure factor and scattering functions of wormlike chain polyelectrolytes and thus help to clarify a longstanding controversy.

### Development of a Multiangle 3D-Cross-Correlation Light Scattering Instrument

Christian MOITZI, Ronny VAVRIN, Suresh BHAT, Anna STRADNER, and Peter SCHURTENBERGER

Static and dynamic light scattering are very popular techniques for the characterization of colloidal suspensions. They provide a wealth of structural and dynamic information on mesoscopic length scales. However, most of the current applications rely on experiments with samples that exhibit single scattering only. This is quite in contrast to the situation encountered when dealing with industrially relevant systems, which are often turbid and thus multiple scattering cannot be neglected.

There exist several DLS schemes to suppress contributions from multiple scattering and to extend the application range of light scattering experiments considerably. In particular the so-called 3D-cross-correlation scheme has been developed during the last few years to an extent that it can now be routinely applied the characterization of turbid for suspensions. These cross- correlation experiments are not only restricted to DLS experiments, but also allow us to extend SLS experiments to turbid systems, as the scattered intensity can be corrected for all



contributions from multiple scattering. However, the experiment duration on classical goniometerbased 3D cross correlation instruments becomes rather long. This often drastically limits our ability to investigate turbid suspensions that exhibit a time dependence such as aggregating or phase separating suspensions.



Therefore а new 3D-cross-correlation instrument was developed, which not only allows for static and dynamic scattering experiments with turbid samples but measures at four angles simultaneously. It thus extends the application of cross-correlation light scattering to time resolved studies where we can efficiently investigate the temporal turbid dispersions. evolution of The combination of multi-angle 3D and on-line transmission measurements is an essential prerequisite for such studies. This not only provides time-resolved information about the overall size and shape of the particles through

measurements of the mean apparent radius of gyration and hydrodynamic radius, but also on the weight-average apparent molar mass via the absolute forward scattering intensity. We developed an efficient alignment strategy based on the novel design of the instrument and tested the application range of the instrument using well-defined model latex suspensions. The effectiveness of the cross correlation multi-angle technique to monitor aggregation processes in turbid suspensions was shown for the acidification of skim milk during the yoghurt making process. Due to the self-assembled nature of the casein micelles an understanding of the sol-gel process induced by the acidification is only feasible if time-resolved light scattering experiments on absolute scale are possible under industrially relevant conditions, where the casein solutions are highly turbid.

C. Moitzi, R. Vavrin, S. K. Bhat, A. Stradner, P. Schurtenberger, submitted to the Journal of Colloid and Interface Science.

#### Fluctuations at the liquid-air interface

#### **Reinhard SIGEL**

In collaboration with

Max Planck Institute of Colloids and Interfaces, Germany (Antonio STOCCO and Klaus TAUER) and Theoretical and Physical Chemistry Institute, Athens, Greece (Stergios PISPAS)



Oil and water do not mix. Instead, a mixture of these liquids separates and a well-defined interface is formed. The incompatibility of aqueous (hydrophilic) and oil-like (hydrophobic) media is a wide spread motive in colloidal systems which leads to structure formation. Examples are found in biological cells, where the cell structure involves a lot of interfaces stabilized by hydrophilic-hydrophobic repulsion and other colloidal interactions. In general, such interfaces are covered by molecules with hydrophilic and hydrophobic parts (amphiphilic molecules).

An apparatus was built to study the behavior of molecules at liquid interfaces by optical methods (see sketch above). The average interface coverage is detected by ellipsometry. Of special interest are fluctuations within the interface, since they contain information about local mobility and in general about the softness of the interfacial structure. A simple but powerful tool for the detection of fluctuations is dynamic light scattering DLS. For suitable illumination geometry under total internal reflection, DLS gets sensitive to fluctuations within the interface.

As a start, capillary waves at a water/air interface were investigated. Their detection by an optical method gives contact-free access to the interface tension, a further important parameter of the interfacial state. The oscillatory behavior of the capillary waves depends on the in-plane scattering vector  $q_{II}$ , which is varied by a change of the detector angle (see figures in middle and right below). For amphiphilic macromolecules at the interface, only a small effect on the capillary waves was detected at low concentration. For higher concentration, the scattering signal is dominated by the diffusion of these molecules, and capillary waves can no longer be detected. The investigation of capillary waves by simple laser light scattering is far superior to X-ray DLS measurements at a synchrotron, since must faster dynamics is accessible and - surprisingly - the maximum  $q_{II}$  where capillary waves can be detected is larger by a factor 10.

Further, a high and narrow intensity peak is observed at the critical angle of total internal reflection  $\phi_0$  (see left figure below). Its location resembles the Yoneda peak, however, its high and narrow shape cannot be explained similar to the Yoneda peak. The occurrence of the peak is discussed as an additional contrast mechanism: directly at  $\phi_0$ , the local bending of the interface by the capillary wave leads to an oscillation between total internal reflection and normal dielectric reflection. Since this mechanism operates only at  $\phi_0$ , the peak is very narrow. A qualitative analysis hints to a second order effect as the origin of the peak. By adding amphiphilic polymers to the interface, the peak weakens and becomes broader. The interfacial refractive index profile affects the height of the peak. Thus, the peak can be used as an additional tool to study liquid interfaces.



#### [1] A. Stocco, K. Tauer, S. Pispas, R. Sigel, European Physical Journal E (submitted).

#### II: Publications 2008

"Soft nanotechnology - from colloid physics to nanostructured functional materials" H. Dietsch, V. Malik, M. Reufer, C. Dagallier, A. Shalkevich, M. Saric, T. Gibaud, F. Cardinaux, F. Scheffold, A. Stradner, P. Schurtenberger Chimia 62, 805 (2008)

"Do equilibrium clusters exist in concentrated lysozyme solutions?" A. Stradner, F. Cardinaux, S. Egelhaaf, P. Schurtenberger PNAS 105:E75 (2008)

"A simple patchy colloid model for the phase behaviour of lysozyme dispersions" C. Gögelein, G. Nägele, R. Tuinier, T. Gibaud, A. Stradner, P. Schurtenberger J. Chem. Phys. 129, 085102 (2008)

"Density-dependent interactions and structure of charged colloidal dispersions in the weak screening regime"

L. F. Rojas-Ochoa, R. Castaneda-Priego, V. Lobaskin, A. Stradner, F. Scheffold, P. Schurtenberger Phys. Rev. Lett. 100, 178304 (2008)

"Improved Cooperativity of Spin-Labile Iron (III) Centers by Self-Assembly in Solution." C. Gandolfi, C. Moitzi, P. Schurtenberger, G. G. Morgan, M. Albrecht J. Am. Chem. Soc. 130, 14434 (2008).

"Magnetic nanoparticles with variable size and shape and surface functionality as switchable building blocks for soft nanotechnology" H. Dietsch, M. Reufer, V. Malik and P. Schurtenberger Proceeding NSTI-Nanotech 1 (2), 226-229 (2008).

"Effects of sample polydispersity and beam profile on ellipsometric light scattering" R. Sigel and A. Erbe Applied Optics 47, 2161-2170 (2008)

"Self-consistent field theory for obligatory co-assembly" I. K. Voets, F. A. M. Leermakers Physical Review E 78, 061801 (2008)

"Complex coacervate core micelles" I. K. Voets, A. de Keizer, M. A. Cohen Stuart Advances in Colloid and Interface Science, DOI:10.1016/j.cis.2008.09.012 (2009)

"Colloidal Characterization and Thermodynamical Stability of Binary Eye Lens Proteins Mixtures" N. Dorsaz, G. Thurston, A. Stradner, P. Schurtenberger, G. Foffi J. Phys. Chem. B (accepted, Web publication December 10, 2008)

"Synthesis and characterization of novel functional electrosterically stabilized colloidal particles prepared by emulsion polymerization using a strongly ionized amphiphilic diblock copolymer" P.S. Mohanty, H. Dietsch, L. Rubatat, A. Stradner, K. Matsumoto, H. Matsuoka and P. Schurtenberger Langmuir (2008, accepted)

"Temperature sensitive poly(N-Isopropyl-Acrylamide) microgel particles: a light scattering study" M. Reufer, P. Diaz-Leyva, I. Lynch and F. Scheffold EPJE (accepted, Web publication November 25, 2008) "Interaction of mono-carboxylic acids in benzene studied by small-angle neutron scattering" V. I. Petrenko, M. V. Avdeev, L. Almásy, L. A. Bulavin, V. L. Aksenov, L. Rosta and V. M. Garamus Colloids and Surfaces A: Physicochemical and Engineering Aspects (accepted)

"Separation of coherent and incoherent scattering contributions in ellipsometric light scattering experiments on latex mixtures" A. Erbe, K. Tauer, and R. Sigel Langmuir (accepted)

"Crystallization in three- and two-dimensional colloidal suspensions" U. Gasser Journal of Physics: Condensed Matter (2008, submitted)

"A New Instrument for Time Resolved Static and Dynamic Light Scattering Experiments in Turbid Media." C. Moitzi, R. Vavrin, S. K. Bhat, A. Stradner, P. Schurtenberger *J. Colloid Interface Sci.* (2008, submitted)

"Dynamical arrest in protein solutions: Can we construct a generalized phase diagram?" T. Gibaud, F. Cardinaux, J. Bergenholtz, A. Stradner, and P. Schurtenberger Phys. Rev. Lett. (2008, submitted)

"Micelle-to-vesicle transition studied by microwave temperature-jumps" M. Zackrisson, E. Norrman and U. Olsson Journal of Physical Chemistry B (2008, submitted)

"Scattering functions of core-shell-structured hard spheres with Schultz-distributed radii" M. Nayeri, M. Zackrisson and J. Bergenholtz Journal of Physical Chemistry B (2008, submitted)

"Dynamics at the air-water interface revealed by Evanescent Light Scattering" A. Stocco, K. Tauer, S. Pispas, and R. Sigel European Physical Journal E (2008, submitted)

"Glycopolymer vesicles with an asymmetric membrane" H. Schlaad, L. You, R. Sigel, B. Smarsly, M. Heydenreich, A. Mantion, and A. Masic ChemComm (2008, submitted)

"Structure-Properties Relationship in Proton Conductive Sulfonated Polystyrene-Polymethyl Methacrylate Block Copolymers (sPS-PMMA)" L. Rubatat, C. Li, H. Dietsch, A. Nykänen, J. Ruokolainen and R. Mezzenga, Macromolecules 41, 8130-8137 (2008).

"Methods for functionalization of microsized polystyrene beads with titania nanoparticles for cathodic eletrophoretic deposition"

S. Radice, P. Kern, H. Dietsch, S. Mischler and J. Michler, Journal of Colloid and Interface Science 318, 264–270 (2008).

# **III: Talks and Posters**

#### Christian Moitzi

Food Colloids Conference, 6-9 April 2008, Le Mans, France Poster presentation "Casein micelles, their structure, interactions and aggregation behaviour revisited"

#### Vikash Malik

Swiss Workshop on Basic Research in Nanoscience, June 4, 2008 Oral presentation "Magnetic core-shell nanoparticles with tailored surface functionality and magnetic properties"

22<sup>nd</sup> Conference of the European Colloid and Interface Society, , Cracow, Poland, August 31 - September 5, 2008 Oral presentation

"Morphology and surface functionality control of magnetic nanoparticles"

#### **Olivier Pravaz**

Soft Matter Composites (Nanocomposites & Polymer Dynamics), Université de Montpellier (UM2) – Montpellier, France, November 27, 2008 Oral presentation "Incorporation of nanoparticles in a polymer matrix: How to synthesize an agglomerate-free nanocomposite?"

#### **Mathias Reufer**

"Liquid Mattter", Lund, Sweden, 27 June - 1 July, 2008 Oral presentation

"Temperature sensitive core-shell particles as a model system to studyequilibrium and non-equilibrium phase behaviour of hard sphere systems"

22<sup>nd</sup> Conference of the European Colloid and Interface Society, Cracow, Poland, August 31 - September 5, 2008

Oral presentation

"Temperature sensitive core-shell particles as a model system to studyequilibrium and non-equilibrium phase behaviour of colloids"

#### Peter Schurtenberger

Research Seminar, Tetrapak - Romont, Switzerland, 12. March, 2008 Invited Seminar "Nanotechnology in Fribourg: The Adolphe Merkle Institute and its facilities" Postgraduate Lecture, Eye Clinic of the University Hospital Zurich - Zurich, Switzerland, 17. March 2008 Invited Lecture "Die Physik der Katarakt oder "Nanophysics goes Bio"

Minisymposium on Food Physics and Soft Matter, Nestlé Research Center - Vers-chez-les-blanc, Switzerland, 19. March, 2008 Invited Lecture "Soft Matter Physics applied to Food Materials"

Physics Seminar, University La Spienza - Rome, Italy, 29 April 2008 Invited Seminar "Proteins seen from a colloid physicists viewpoint"

General Public Lecture, "Turmklub Malters" - Malters, Switzerland, 28 May 2008 Invited Lecture "Nanotechnologie zwischen Science Fiction und Alltag"

Nanotech 2008 - Boston, USA, June 1 - 5, 2008 Invited Keynote Lecture "Soft nanotechnology - from soft matter physics to food and materials sciences"

9th European School on "Scattering Methods Applied to Soft Condensed Matter" - Bombannes, France, 8. – 13. June 2008 Invited Lecture "General Introduction to Scattering Experiments"

9th European School on "Scattering Methods Applied to Soft Condensed Matter" - Bombannes, France, 8. – 13. June 2008 Invited Lecture "Aggregation, Sol-Gel Transition and Glasses"

7th Liquid Matter Conference - Lund, Sweden, 27 June - 1 July 2008 Invited Keynote Lecture "Equilibrium and non-equilibrium phase transitions in protein solutions - exploring the colloid analogy"

XVth International Congress on Rheology - Monterey, USA, August 3-8, 2008 Oral Presentation "Intriguing two-time-scale elasticity in arrested phases of lysozyme solutions"

Fall Meeting of the Swiss Chemical Society - Zurich, Switzerland, September 11, 2008 Invited Lecture "Soft nanotechnology - from colloid chemistry to nanostructured functional materials"

Nanotech Northern Europe 2008 - Copenhagen, Denmark, 23 - 25 September 2008 Invited Keynote Lecture "Application of concepts from colloid physics to food technology"

SLS Seminar, Paul Scherrer Institute - Villigen, Switzerland, 26 September 2008 Invited Seminar "Soft matter goes nano - From colloid physics to nanostructured materials" Institute of Chemistry Seminar, University of Campinas - Campinas, Brazil, September 30, 2008 **Invited Seminar** 

"Micelles as "equilibrium polyelectrolytes": The interplay between interactions, micellar growth and rheological properties"

LNLS Seminar, Brazilian Synchrotron Light Laboratory - Campinas, Brazil, October 2, 2008 **Invited Seminar** "Small-angle scattering experiments applied to soft matter"

Institute of Chemistry Seminar, University of Sao Paulo - Sao Paulo, Brazil, October 7, 2008 **Invited Seminar** "Colloids - From model atoms to novel materials"

AutoOrg 2008 - Sao Pedro, Brazil, October 9 2008 Invited Lecture "Aggregation, phase separation and gel formation in biocolloid and biopolymer solutions"

Material and Chemical Research Seminar, Industrial Technology Research Institute (ITRI) - Hsinchu, Taiwan, October 21, 2008 **Invited Seminar** "Colloid chemistry - From model atoms to nanostructured materials"

Department of Chemical Engineering Seminar, National Tsing Hua University - Hsinchu, Taiwan, October 23, 2008 Invited Seminar

"Gaining insight into protein structure and interactions from small-angle scattering experiments"

NSRRC Seminar, National Synchrotron Radiation Research Center - Hsinchu, Taiwan, October 24, 2008 **Invited Seminar** 

"Gaining insight into protein structure and interactions from small-angle scattering experiments"

Cercle Politique et Economie - Chateau de Seedorf, November 5, 2008 Invited Public Lecture "Nanotechnology and Technology Transfer at the University of Fribourg"

BASF Physics Colloquium - Ludwigshafen, November 10, 2008 Invited Seminar "Concentrated colloidal suspensions, glasses and gels"

CTI Micro and Nano Technologies Event 2008 - Neuchatel, 11 November 2008 Invited Lecture "Nanomaterials: A new avenue for enterprises?"

Hercules Specialized Course on "Scattering and Imaging Studies of Soft Matter Systems using Synchrotron Radiation and Neutrons" - Grenoble, November 17, 2008 Invited Lecture

"Small-angle scattering experiments applied to soft matter"

#### **Reinhard Sigel**

Liquid Matter 2008, June 27 - July 1, Lund, Sweden Poster presentation "Structure of Amphiphilic Polyisoprene-Poly(ethylene oxide Block Copolymers in Very Dilute Aqueous Solution"

Jülich Soft Matter Days 2008, November 11 - 14, Bonn, Germany Poster presentation "High resolution ellipsometric studies on bare fluid interfaces"

Jülich Soft Matter Days 2008, November 11 - 14, Bonn, Germany Poster presentation "Structure of Amphiphilic Polyisoprene-Poly(ethylene oxide Block Copolymers in Very Dilute Aqueous Solution"

#### Anna Stradner

Universität Tübingen, Institut für angewandte Physik – Tübingen, Germany, November 18, 2008 Invited Seminar "Proteins as model colloids: new insight into lens transparency and cataract formation"

7th Summer School on Condensed Matter Research - Zuoz, Switzerland, August 16-22, 2008 Invited Lecture "Colloids: From Model Atoms to Nanostructured Materials"

NSTI Nanotechnology Conference - Nanotech 2008 - Boston, Massachusetts, USA, June 1-5, 2008 Invited Keynote Lecture "New Routes to Gels and Glasses, or How to Apply Analogies between Soft Matter Physics and Food Systems"

Meeting of the 'Association des Amis de l'Université de Fribourg'- Zürich, Switzerland, May 28, 2008 Invited Public Lecture "Nanowissenschaften zwischen Science Fiction und Alltag"

SoftComp Annual Meeting - Riva del Garda, Italy, May 5-9, 2008 Invited Plenary Lecture "Structure and Dynamics of Colloidal Gels and Glasses"

12th Congress of Food Colloids - Le Mans, France, April 6-9, 2008 Oral Presentation "New Routes to Gels and Glasses"

#### Kitty van Gruijthuijsen

Swiss Workshop on Basic Research in Nanoscience - Davos, Switzerland, June 4-6, 2008 Poster presentation "Depletion interactions in aqueous, charged colloid-polymer mixtures"

Final conference of the EU RTN Arrested Matter on Dynamical Arrest of Soft Matter and Colloids -Taormina, Italy, November 22-26, 2008 Oral presentation "Dynamical arrest in a phase-separating food colloid-biopolymer mixture"

#### Malin Zackrisson

7<sup>th</sup> Liquid Matter Conference, Lund, Sweden, June 27 –1 2008 Poster presentation "Reversible aggregation of PEG-grafted colloids"

Polyelectrolytes 2008, Coimbra, Portugal, June 16-19 2008 Poster presentation "Structure and stability of eye lens protein mixtures"

# **IV: Selected Memberships in External Committees**

#### Peter Schurtenberger

Member of the Swiss National Research Council (Division IV "Targeted Research")

General Secretary of the European Colloid and Interface Society

Member of the Liquids Board of the European Physical Society

Editorial Board, Journal of Physics: Condensed Matter, Liquids, Soft Matter and Biological Physics Board

Editorial Board, Colloid & Polymer Science

Section Editor, Current Opinion in Colloid and Interface Science

Advisory Board (Kuratorium), "Physik in unserer Zeit"

Swiss Representative in the Management Committee of COST Action D43

Swiss Representative in the Scientific Council of the Institute Laue-Langevin

Member of the Program Committee of SoftNano2008, International Conference on Nanostructured Fluids, Soft Materials & Self-Assembly, Nanotech 2008, 1. - 5. June, 2008, Boston, USA

Conference chair, Nanoparticles in Soft Materials, Special Symposium in Nanotech2008, 1. - 5. June, 2008, Boston, USA

Member of the organizing committee, 9th European Summer School on "Scattering Methods Applied to Soft Condensed Matter", Bombannes, France, 8. – 13. June 2008

#### Anna Stradner

Member of the Scientific Committee of the Swiss Spallation Source SINQ at the Paul Scherrer Institute (PSI)

Member of the selection committee for a Professorship at ETHZ and PSI in Experimental Condensed Matter Physics and Head of Laboratory for Neutron Scattering

Member of the Scientific Advisory Committee of the 23<sup>rd</sup> Conference of the European Colloid and Interface Society, Antalya, Turkey, 6 - 11 September 2009

Member of the Scientific Advisory Committee of the XIV International Conference on Small-Angle Scattering, Oxford, UK, 13 - 18 September 2009

### V: Visitors

Esther Groeneveld (Master Student) Condensed Matter and Interfaces Ornstein Laboratory University of Utrecht Princetonplein 1 Utrecht The Netherlands 5 Months research stay for external Master thesis(March – August)

#### Marc Obiols Rabasa (PhD Student)

Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN) Institut d'Investigacions Químiques i Ambientals de Barcelona (IIQAB) Consejo Superior de Investigaciones Científicas (CSIC) C/Jordi Girona 18-26 08034 Barcelona Spain 3 Months research stay for external Master thesis 1. May 2008 – 31. July 2008

Investigation of colloidal dispersions (polybutyl acrylate, polystyrene and poly(MMA/BuA)) stabilized by a sugar-derivative polymeric surfactant. The stability with different electrolytes (KBr, CaCl<sub>2</sub> and MgSO<sub>4</sub>) was determined by dynamic light scattering in terms of the Stability Ratio and the Critical Coagulation Concentration (CCC).

#### Prof. Johan Bergenholtz

Physical Chemistry Department of Chemistry Göteborg University SE-41296 Göteborg Sweden Phone: +46 317722748 Email: jbergen@chem.gu.se 05.05.2008 – 09.05.2008

Simon Küster (Master Student) Rochusstrasse 48 52062 Aachen Germany Email: simon.kuester@rwth-aachen.de 24.11.2008 – 23.01.2009

#### PD Dr. Peter Lang

Forschungszentrum Juelich Institut für Festkörperforschung 52425 Juelich, Germany 5.5.-6.5. 2008 Seminar "Near wall dynamics and interaction potentials in colloidal supensions"

#### Lisa Maus und Roberto Fiammengo

Max-Planck-Institut für Metallforschung Abteilung Neue Materialien und Biosysteme

#### Prof. Spatz

Heisenbergstr. 3 70569 Stuttgart 2.-4.12. (Light and X-ray scattering characterization of coated gold colloids).

#### Prof. Markku Kulomaa

Institute of Medical Technology University of Tampere Tampere, Finland 27 November 2008 Seminar: Engineering and design of "New Brave Avidins"

# VI: Short Term Collaborations with Universities and Industry

#### Prof. Martin Albrecht, Claudio Gandolfi

University of Fribourg, Chemistry Department, Ch. du Musee 9, 1700 Fribourg, Switzerland Self-assemply of Fe(sal<sub>2</sub>trien) complexes investigated by dynamic light scattering and small angle x-ray scattering.

"Improved Cooperativity of Spin-Labile Iron (III) Centers by Self-Assembly in Solution." C. Gandolfi, C. Moitzi, P. Schurtenberger, G. G. Morgan, M. Albrecht, *J. Am. Chem. Soc.* **130**, 14434 (2008).

Prof. Katharina Fromm

University of Fribourg, Chemistry Department, Ch. du Musee 9, 1700 Fribourg, Switzerland Dynamic light scattering and small angle x-ray scattering of one dimensional coordination networks of  $AgNO_3$  and ditopic ligands.

#### Dr. Ana Borras

EMPA Thun, Laboratory for nanotech@surfaces, Feuerwerkerstrasse 39, 3602 Thun, Switzerland Small angle x-ray scattering of PtOEP and CuPHTH fibers grown on glass substrate by plasma CVD.

Prof. Paul Bruehwiler

EMPA St.Gallen, Laboratory for Protection and Physiology, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland

The crystallization of pure Polyamide-6 fibers drawn at different draw ratios and fibers with a low concentration of MWCNT were studied by small and wide angle x-ray scattering.

Dr. Sebastien Guimond EMPA St.Gallen, Laboratory for Plasma-modified Surface, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland Structural investigations of nanocomposite Ag/plasma polymer thin films by small angle x-ray scattering.

Brian Codery, Sara Davies Bristows, 100 Victoria Embankment, London, GB / Novartis AG Analysis of the droplet size distribution of Deximune 100 Cyclosporine samples by small angle x-ray scattering.

Dr. Xin Gao, Dipl. Ing. Thierry Jomini Frewitt SA, Route du Coteau 7, 1763 Granges-Paccot, Switzerland Analysis of the particle size distributions of iron oxide particle dispersions by dynamic light scattering.