





# Research in the Department of Interfaces

## I. General Strategy

Interfaces are most important on one hand to understand and control colloidal systems with their large fraction of specific surface, on the other hand most processes start at an interface, and therefore they determine many physical and chemical properties. From a basic science point of view they exhibit peculiarities as low-dimensional systems' and are anisotropic systems where molecules can be oriented. Within the institutes' strategy of building and understanding hierarchical structures they are positioned at the lowest length scale which one may also consider the base. Accordingly the main aim of the department is to understand and to control molecular interfaces as regards structure, dynamics and properties. As an offspring of this the knowledge could be used to prepare complex films, coated colloids and capsules. For this the department has established a zoo of techniques to characterize colloids and interfaces and, especially concerning studies of liquid interfaces, we are probably best equipped world-wide.

As a general trend in all groups the interfaces increase in complexity, i.e. planar interfaces mostly also contain proteins, polypeptides or nanoparticles. If the interface contains only small molecules the dynamics is of prime importance. A sole exception of the above are studies concerning the old and new problem of water structure at the interface and the arrangement of peculiar groups like  $\text{CF}_2$  at interfaces.

On the other hand the mission is also to concentrate on basic science and therefore schemes had to be developed to transfer technology and knowledge to groups and partners oriented towards application.

The research concerns predominantly experiments between chemistry and physics with little molecular synthesis and biology, and also theory is mostly employed only in collaborations. It is organized within ten groups which are largely independent from the director but interact with me in varying intensity. Some scientists are also under my direct supervision which is in special necessary if the group leader has left or if there is a topic to be taken up independent of the immediate interest of a specific group.

## II. Research Highlights

### II. 1 Planar Interfaces

Insoluble monolayers at the air/water interface as most suitable model system are made use of in the group of *G. Brezesinski* studying polypeptides, phospholipids, DNA binding and enzymatic hydrolysis and phosphorylation at interfaces, the leading techniques being FTIR-

spectroscopy and X-Ray scattering. It is demonstrated for  $\beta$ -amyloid that it changes structure and orientation depending on the lipid density at an interface it is coupled to. For an antibiotic peptide it is shown that it assumes an  $\alpha$ -helical conformation upon membrane insertion and at the same time

fluidizes the membrane. For studies of peptides successful collaboration with the theory (*V. Knecht*) and the colloid chemistry (*H. Börner*) departments could be developed. The structure, but even more the presence of domain boundaries in lateral phase separation of mixed phospholipid/ cholesterol mixtures has been shown to affect the activity of phospholipases.

The group of *H. Motschmann* could demonstrate by sum frequency spectroscopy that the thiocyanate ion, as a representative chaotropic ion where the interfacial orientation can be determined, affects the water structure at the surface. Its orientation has to be taken into account because most probably a dipolar interaction disorders the water structure.

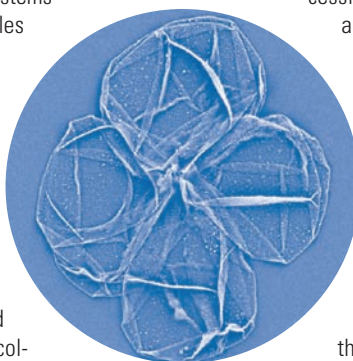
The slow dynamics ( $< 1$  Hz) of mixed protein/surfactant adsorption layers has been the focus of the group of *R. Miller*. They could describe the dilational modulus as a function of frequency for different composition within a model they derived. The group now has also expanded their models to describe the thermodynamics of nanoparticles at fluid interfaces.

Interactions between liquid interfaces and local dynamics are the main topics of the group of *R. Krastev*. For foam films they showed that their drainage can be described by classical theories only down to thicknesses of 40nm. For lower thickness the velocity increases more drastically than expected for constant friction. For polyelectrolyte multilayers containing a phospholipid bilayer they showed that lipid coupling reduces the water content of the multilayer.

Alkanes on solid ( $\text{SiO}_2$ ) surfaces have been the prime interest of the group of *H. Riegler*. These systems are most simple models since they are expected to exhibit only van der Waals interactions. It has been shown that the surface induces crystallization, and the extent is determined by the  $\text{SiO}_2$  thickness. Thus studying the melting point increase the interaction potentials could be derived.

### II. 2 Non – Planar Interfaces

The hierarchical assemblies of bisterpyridines, metal ions and amphiphiles studied in the group of *D. Kurth* have gained increasing interest and complexity due to the dynamic nature of the modules. Since the molecular weight of the metal containing polyelectrolyte drastically depends on the stoichiometry of the partners this dependence had to be modeled (coop. *T. Gruhn* theory) and studied in detail by analytical centrifugation (coop. *H. Cölfen*, colloid chemistry). As transitions between the phases are accompanied by changes in the coordination geometry they also affect the optical and magnetic properties.





The group of *G. Sukhorukov* has shown the existence of temperature induced shape transitions in polyelectrolyte multi-layer capsules. Since the high temperature phase is distinguished by high mobility an equilibrium structure concerning capsule dimensions could be established. It results from a minimization of the surface energy balancing hydrophobic and electrostatic contributions. The latter can be manipulated in a predictable way via pH and salt. It was also shown that capsules can be sensitized toward IR absorption to enable remote release at specific location within a cell.

The glass transition within multilayers has also been verified and quantified by AFM based elasticity measurements in the group of *A. Fery*. At the transition which can be varied via salt and type of polyelectrolyte between 20°C and 90°C the modulus changes by more than two orders of magnitude.

*D.G. Shchukin* has developed sonochemistry as a new way to prepare multifunctionalized nanocontainers. He also managed to show how to integrate electrochemically responsive containers into coatings.

The group of *D. Wang* functionalizes nanoparticles to direct their organization on different length scales. It is shown that Au nanoparticles can be reversibly switched via pH to move between different solvents and their interface. Arrays of nearly  $\mu\text{m}$  sized capsules can on the other hand be used to pattern surfaces or to coat colloidal particles such that they exhibit symmetric interactions into 3D such as  $\text{sp}^2$  or  $\text{sp}^3$  hybrids.

The control of vectorial electron transfer across thin films and capsule walls has been an issue for a joint effort with TU Berlin (*P. Hildebrandt*) and University Potsdam (*F. Scheller, R. Menzel*) with participation of the groups of *R. Krastev* and *D. Kurth*. There it was shown that electron transfer between chromophores, even if they are 3 nm apart is not mediated by conjugated bonds. The electron transfer between redox active proteins in films is shown to occur directly between these molecules which may provide a means to construct highly specific sensors.

The International Joint Laboratory with the CAS led by *J. Li* has been successful creating capsules existing of polyelectrolytes, phospholipids and the membrane integral channel and motor ATP ase. It could be shown that thus a pH gradient could be converted into ATP.

The collaborative research group together with the Fraunhofer IAP has been active as a partner in surface functionalization of nanoparticles as well as in the synthesis of block copolymers to functionalize planar and curved surfaces. It has been successful in establishing a Campus project on "Bioactive Surfaces" including also the newly settled Fraunhofer Institute of Biomedical Technology.

### III. Future Development

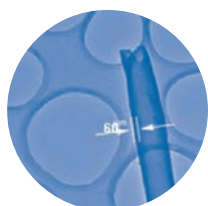
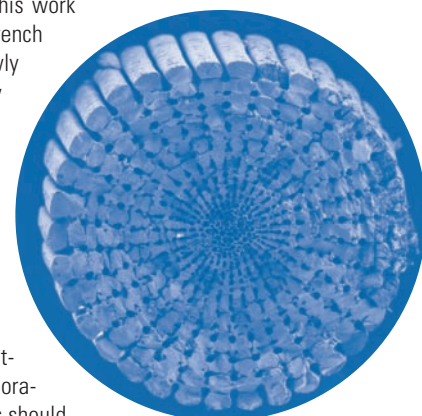
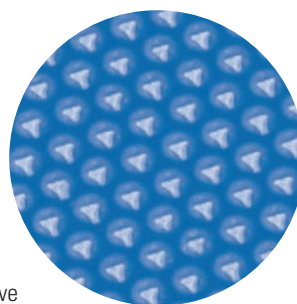
Major changes at the level of staff scientists in the last two years have been:

- *D. Wantke* retired, and a part of his activities have been taken over by the group of *H. Motschmann*
- *A. Fery* has accepted a call to move as professor to the University Bayreuth. His group will cease to exist during this year with 1 or 2 postdocs remaining in the department continuing collaboration with him.
- The group of *G. Sukhorukov* will also expire during this year with the last thesis finishing. Some activities with microcapsules will, however, be continued within the department with postdocs and guests directly associated with the director.
- Towards beginning of next year also *D. Kurth* is expected to leave the department. To continue the activities on supramolecular systems as well as the joint laboratory with NIMS T. Nakanishi has started to work here as group leader.
- *D. Shchukin* won the Nanofuture award which enables him to build-up an own group on self-repairing coatings within the department. Mostly under the guidance of *D. Shchukin* we have also started research towards sonochemistry, the conversion of surface energy into chemistry. This work will be expanded within a joint German/ French laboratory, the French partner being the newly established institute for separation chemistry headed by *T. Zemb* at Marcoule (CEA). In order to intensify this collaboration I have received also the Gay-Lussac award jointly from the French ministry of science and technology and the Humboldt foundation.

Altogether, topics just emerging in the department are sonochemistry and self-repairing coatings, the other themes are in the phase of harvesting. Therefore national and international collaborations have been established. These collaborations should enable a scientific output even increasing although the headcount is expected to decrease from more than 80 to less than 70 persons. Also I expect that this way the funding by EU projects (participation in 6 STREP in the 6<sup>th</sup> framework programme) may be kept at the same level. Another focus will be to make the campus project "Bioactive Surfaces" a success which means to concentrate studies on molecular interfaces more towards surfaces responsive to switch attachment and function of proteins and cells.

That much of the research is interesting, original and modern the reader may deduce from the next pages. Measuring the success in funding and citations is now fashionable, easy and only partly correct. Although these numbers are very favourable I refrain from listing them because of their limited value. The most important criterion in my view is that many students and postdocs could make a major step in their career which in turn makes further thriving the field of molecular interfaces.

Helmuth Möhwald  
Director of the Department of Interfaces



## Interactions at Interfaces: Langmuir Monolayers as Model Systems



Monolayers provide a flexible and versatile system to study interactions at surfaces, especially those relevant to biological systems. The behavior of biomolecules, such as lipids, peptides, and DNA, confined in a surface environment can be studied using single- or multi-component monolayers [1-3].

### Peptide-Lipid Interactions

Smaller peptides and model systems allow us to study fundamental interactions such as electrostatic effects, hydrophobic interactions, or packing constraints that control peptide behavior at surfaces. The packing and charge density of a monolayer can be easily varied to study the effect of surface composition on peptide behavior.

Small model  $\beta$ -sheet forming peptides are one area of our current focus [2,4,5]. This focus stems from their assumed role in diseases (amyloid, peptide of Alzheimer's disease) and novel applications of  $\beta$ -sheet self assembly at the air-water interface. Shorter model peptides allow collaborations with colleagues in the Theory department who perform molecular dynamics simulations and with colleagues in the Colloid department who use peptide self assembly to form novel structures.

Another field of peptide research deals with peptide antibiotics. We use the antimicrobial peptide NK-2, which is a 27 amino-acid residues derivative of the cationic core region of NK-Lysin, a polypeptide of mammalian lymphocytes. A better understanding of the mode of action of these peptides could enhance the design and development of alternatives to the conventional antibiotics.

**Results:** Infrared Reflectance Absorbance Spectroscopy (IRRAS) and Grazing Incidence X-Ray Diffraction (GIXD) are used to follow the behavior of small  $\beta$ -sheet forming peptides confined in an interfacial environment. Changes in the conformation and orientation of peptides and novel polymer peptide compounds are studied by a combination of traditional IRRAS measurements at the air-water interface, spectral simulations, and 2D IR correlation techniques. **Fig. 1** shows infrared spectra for a peptide,  $G(VT)_5$ , monolayer in an expanded and highly compressed state. The large increase in only the Amide II band between these two spectra indicates that upon monolayer compression, the  $\beta$ -sheet domains of the

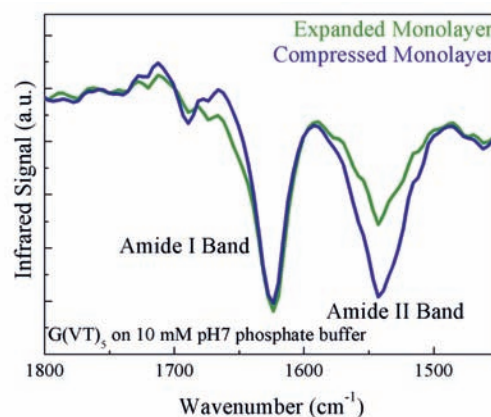


Fig. 1: IRRAS spectra of a  $G(VT)_5$  peptide spread on 10 mM pH 7 phosphate buffer. The spectra were taken at 20 °C using *s*-polarized light and an incident angle of 40°. The surface pressures of the expanded and compressed monolayers were 1 and 44 mN/m, respectively.

$G(VT)_5$  peptide change their orientation in the air-water surface plane. Monolayers of pure  $\beta$ -sheet forming peptides are highly crystalline with 2D order. GIXD measurements show the characteristic spacing, 4.76 Å, for  $\beta$ -sheet structures. Additionally, GIXD measurements at higher pH values show that this structure is conserved even when short chains of *pnBA* (poly(*n*-butyl acrylate) polymer are attached to the peptide, whereas no film structure is seen at low pH. The pH can be used as a switch for this polymer-peptide. The polymer-peptide layers however remain in a fluid like phase unlike the highly crystalline pure peptide film. For the pure peptide film, a Bragg peak that corresponds to a repeat distance equal to the peptide end-to-end distance (45 Å) confirms the crystalline nature of this monolayer.

Adsorption and secondary structure of NK-2 at the air/buffer interface were measured by IRRAS. The peptide reorients from random coil in bulk (CD data) to  $\alpha$ -helical structure at the interface. The long axis of the helix is oriented horizontally to the interface. NK-2 adsorption to an anionic monolayer leads to a fluidization of the aliphatic chains (increased transition pressure). The secondary structure of the adsorbed peptide is different (either  $\alpha$ -helical with an oblique orientation or random coil) from that observed at the air/buffer interface.

GIXD experiments show that the presence of NK-2 influences the structure of the condensed anionic monolayer. The insertion of NK-2 increases the tilt angle of the lipid molecules.

To assess the location of NK-2 in the lipid matrix, specular X-ray reflectivity (XR) studies were performed. The XR curves are shown in **Fig. 2** with the corresponding electron density profiles. The electron density profile shows that NK-2 adsorbs to the negatively charged monolayer even at high surface pressures.

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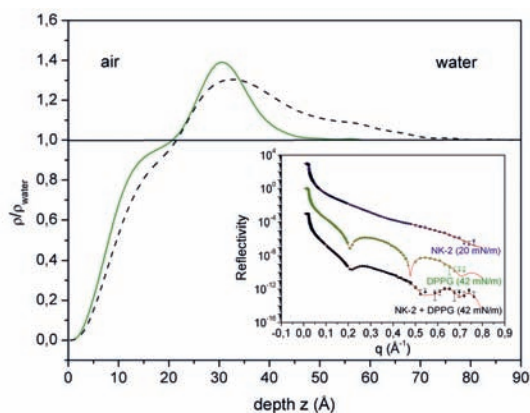


Fig. 2: Electron density profile of 1,2-dipalmitoyl-phosphatidylglycerol (DPPG) on buffer (green line) and on 1  $\mu\text{M}$  NK-2 (black, dashed line) at 42 mN/m and 20  $^{\circ}\text{C}$ . X-ray reflectivity profiles (insert) of 1  $\mu\text{M}$  NK-2 in PBS (10 mM, pH 7.3) adsorbed at the air/buffer interface, DPPG monolayer on PBS and on 1  $\mu\text{M}$  NK-2. Solid lines (red) are the best fits to the experimental data.

### Enzymatic Reactions at Interfaces

The application of surface-sensitive techniques permits *in-situ* observations of particular interactions that occur at biological membranes. Thus, the hydrolysis of phosphatidylcholines by different phospholipases can be investigated. We obtained new results on the dependence of the lipid monolayer structure on the action of phospholipase D (PLD) and phospholipase A<sub>2</sub> (PLA<sub>2</sub>). Another project, which has been recently started in cooperation with the University of Jena, examines the interaction of the phosphatidylinositol 3-kinase  $\gamma$  (PI3K $\gamma$ ), which phosphorylates their substrates, with lipid model membranes.

**Results:** The PLD activity depends on the segregation of the hydrolysis product (phosphatidic acid, PA) within the monolayer. However, no specific structural parameter of the substrate-containing phase, such as the tilt of the lipid chains or the molecular area per head group, is crucial for high hydrolysis rates. Instead, we discovered that the structure of the PA-rich domains is decisive for the activation or inhibition of PLD.

PLA<sub>2</sub> exhibits maximum activity in the simultaneous presence of liquid-expanded and condensed phases. It is therefore concluded that phase boundaries play a crucial role in this process. We revealed that liquid-liquid immiscibility as found in mixed phospholipid/cholesterol monolayers is sufficient to activate the enzyme. This finding involves important progress in the comparison of biophysical observations with physiological conditions as biological membranes naturally occur in a liquid-disordered phase. The eventual formation of liquid-ordered structures implies the occurrence of membrane domains even though the existence of the so-called rafts is still under debate.

The substrates (phosphoinositides) of PI3K $\gamma$  have been shown to mediate a large variety of important physiological functions. The properties of phosphoinositides are largely determined by the structure of their head group, which is at physiological pH highly charged but also able to be engaged in intermolecular hydrogen bond formation. One factor that is expected to affect mutual phosphoinositide interactions is the presence of cations with different valence, size, and concentration [6,7].

The DP-PI3P film becomes progressively more expanded with increasing concentrations of monovalent cations (Li<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>). The tilt angles of the lipids change with the size of the hydrated monovalent cation according to the Hoffmeister series (Fig. 3). Smaller hydrated monovalent cations penetrate deeper into the head group region and increase therefore the area occupied by the head groups and the tilt of the molecules. Divalent cations (Mg<sup>2+</sup> and Ca<sup>2+</sup>) have a strong condensing effect on the inositide monolayer (Fig. 3) and decrease the layer compressibility. The strong influence of Ca<sup>2+</sup> on DP-PI3P can be explained by a partial dehydration of the PI3P head group and a subsequent complex formation.

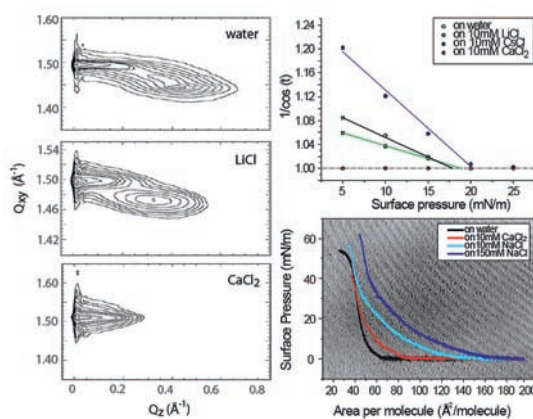


Fig. 3: Left: Contour plots of the corrected X-ray intensities of a DP-PI3P monolayer on different subphases at 10 mN/m. Right: Tilt angle ( $1/\cos(t)$ ) versus lateral pressure (top). BAM picture showing defects within the condensed lipid film with isotherms on different subphases (bottom).

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## Thin Soft Films



When matter is organised in very thin layers (films) the interactions between the film interfaces influence its behaviour. The main aim of our studies is to understand how the strength of the interaction forces modifies the properties of these very thin films. Three types of films are objects of our studies: The foam films – liquid layers which separate two gas phases, wetting films – liquid layers between a gas and solid phase and polymer (polyelectrolyte) films on solid support.

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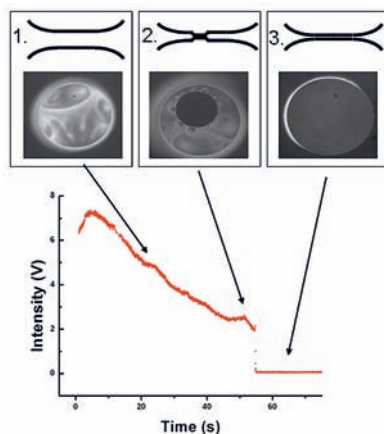
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## Foam Films

Besides the wonderful play of colours which fascinates children, foam films supply important information about the interaction between fluid (gas/liquid or liquid/liquid) interfaces. We intend to understand how the properties of liquids change when they are confined between two interacting surfaces. Our approach is based on studies of the thinning dynamics of foam films (**Fig. 1**). The foam films consist of an aqueous core sandwiched between two adsorbed surfactant layers. They are generally prepared from a drop of an aqueous surfactant solution. Under the action of capillary pressure ( $P_C$ ) and attractive interaction forces between the film surfaces, the liquid is expelled from the drop and a film is created. The film thickness,  $h$ , decreases until the equilibrium is reached. Usually the thinning process is monitored by measuring the intensity of light reflected from the film with the time,  $t$  (**Fig. 1**).



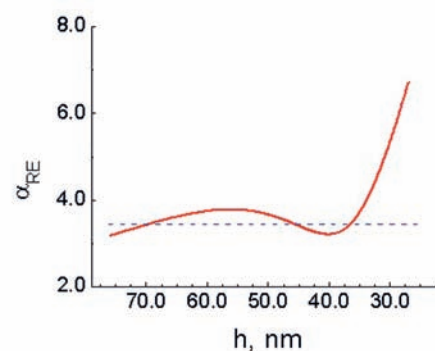
**Fig. 1:** Intensity of light reflected from the film is directly related to the film thickness. When measured as a function of time it is related to the film thinning dynamics. 1. Thinning foam film; 2. Thinner black spots are formed in the film as a result of the film thinning; 3. The black spots expand, cover the whole film and an equilibrium black foam film is formed.

The thinning of a liquid film between two parallel circular solid disks driven by the pressure  $P_C$  is given by the Stefan-Reynolds equation which was later expanded by Scheludko for the case of a disjoining pressure,  $\Pi$ , contribution to the driving force of the thinning:

$$\frac{dh^{-2}}{dt} = \frac{4}{3\eta r^2} (P_C - \Pi(h)) = \alpha_{RE} (P_C - \Pi(h))$$

here  $\eta$  is the viscosity,  $r$  is the radius of the film and  $\alpha_{RE}$  is the Reynolds coefficient. The model is very simple and does not include disturbances related to the mobility or inhomogeneities of the film surfaces. Even though it gives reliable results about the disjoining pressure in the film if the viscosity of the liquid is known.

We performed first experiments on thinning dynamics of foam films stabilised by the non-ionic sugar based surfactant Dodecyl Maltoside ( $C_{12}G_2$ ) at different surfactant concentrations and a constant salt concentration (0.2M NaCl) which assures the formation of very thin black films. We observed that the film thinning follows the Reynolds-Scheludko relation. The coefficient  $\alpha_{RE}$  was constant according to the prediction of the equation in a large range of thicknesses down to 40nm. Below this film thickness a strong deviation was observed. The result does not depend on the surfactant concentration. This shows that application of more complicated models for the film thinning which include the surface mobility of the film interfaces will not change the observed effect **[1]**. An example of the dependence of  $\alpha_{RE}$  on the film thickness is shown on **Fig. 2**.



**Fig. 2:** The Reynolds coefficient  $\alpha_{RE}$  as a function of  $h$  (red line) for films prepared from 0.06 mM  $C_{12}G_2$  and 0.2 M NaCl. Well pronounced deviation from the linear dependence (blue line) is observed in the range of film thickness below 40 nm. The non-linearity above 40 nm is due to the oscillations of the film surfaces deviating from the condition of parallel disks.

One of the main problems when foam films are studied is the position of the planes of interaction, respectively the thickness of the different layers which form the film. The use of various scattering (reflectivity) techniques allows different tuneable contrast between the layers of the film to be achieved. This way the detailed structure of the film can be found, and the data may be used for precise estimation of the interaction between the film surfaces. We performed first neutron reflectometry experiments with foam films stabilised by tetraethyl ammonium perfluoro-octane sulfonate (TAPOS). The contrast between the aqueous film core and the adsorbed surfactant layers was achieved by preparation of the films from D<sub>2</sub>O solutions. High quality reflectivity curves were obtained (Fig. 3). The detailed structure of the film was found and the position of the counter ions in the film was predicted. Well-defined off-specular signal was registered which is related to correlated oscillations on the film surfaces.

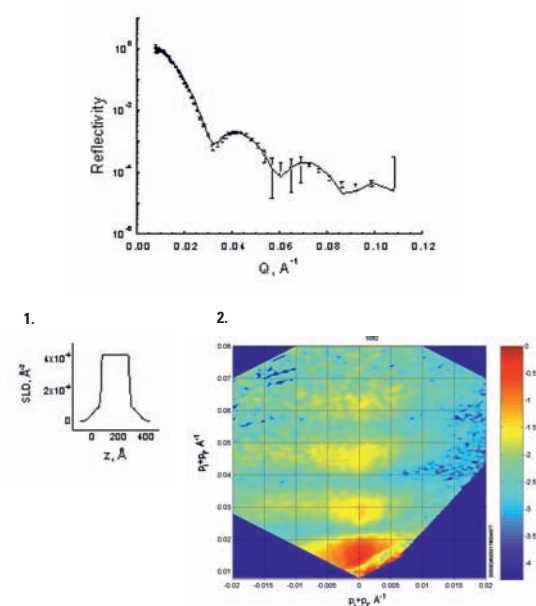


Fig. 3: Neutron reflectometry curve for a foam film prepared from TAPOS. 1. Scattering length density (SLD) profile which gives the best fit to the data; 2. Well-pronounced off-specular signal from the film.

### Wetting Films

We studied the stability of aqueous wetting films on hydrophobic support (Teflon) [2]. The studies are important when the formation of a three phase contact between solid, liquid and gas phase is concerned. The film stability depends on the acting forces and delivers information about them. We observed a relation between the roughness of the solid phase and the aqueous film stability. Increasing the roughness of the solid support leads to decrease in the film stability. This confirms the strong influence of microscopic gas bubbles entrapped at the solid interface on the film stability. The stability is governed by the interactions of the liquid/air interface with these bubbles. Microscopic foam films are formed instead of direct contact with the solid surface.

### Polyelectrolyte Films on Solid Support

The aim of our studies was to understand more about the thermodynamics of thin polymer layers deposited on solid support and to use them as a support to prepare composite materials including layers with different hydrophobic or surface (bio-) active molecules. The thin polymer layers were prepared from polyelectrolytes (PE) organised in multilayers (PEM) using the layer-by-layer dipping deposition technique. We studied the deposition of lipid molecules onto PEM and showed that formation of composite lipid/PEM structures is possible. The process depends on the charge of the PEM and the lipid molecules [3]. This proved that the formation of the composites is driven by electrostatic interactions. Proper conditions allowed formation of sandwich like structures composed of a lipid bilayer between two blocks of PEM (Fig. 4).

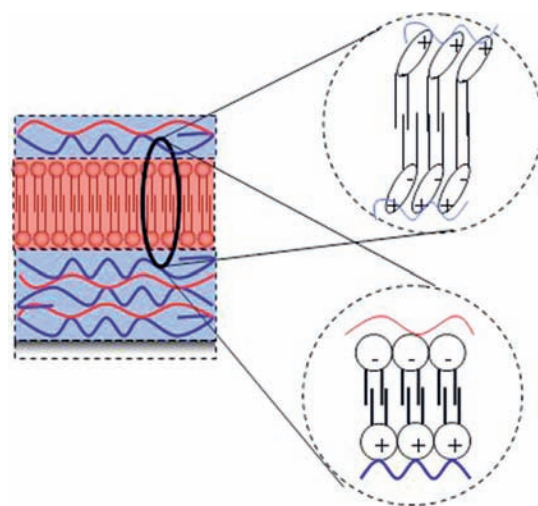


Fig. 4: Lipid layers cushioned onto hydrated PEM. Formation of sandwich like structures or bilayers with asymmetric charge distribution was possible.

Formation of asymmetric lipid layers was also successful which makes possible preparation of composite PEM with separated charges. The difference in the charge density and the hydrophobicity in the structure of such composite PEM will be used in the future to develop new complex materials. Inclusion of a lipid layer leads to decrease in the water content of the PEM. We expect that the effect is related to the modified interactions in the PEM (studies in progress). This effect could be used in future experiments to prepare layers with precisely tuned hydration.

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## Dilational Rheology of Mixed Protein-Surfactant Adsorption Layers



The addition of surfactants can significantly modify the properties of adsorbed protein layers at liquid/fluid interfaces, leading to changes of the adsorption and rheological characteristics. Although the dilational rheology of proteins or protein/surfactant mixtures is extremely important from a practical point of view, a general theory is still not available. For the much simpler mixtures of two surfactants it appeared to be possible that the rheological behaviour can be described using data for the individual components. The very first attempts to analyze theoretically the rheology of surfactant mixtures were made for example by Lucassen-Reynders, Garrett and Joos. Recently we succeeded in further developing the given theoretical model such that it became applicable to experimental equilibrium and dynamic surface pressure data, for surfactant mixtures as well as for protein-surfactant mixtures [1]. For the high frequency limit the thermodynamic quantities are sufficient to describe experimental visco-elasticities [2,3]. In this report we describe results of experimental studies of the dilational rheology of a  $\beta$ -lactoglobulin (BLG) mixture with the nonionic surfactant decyl dimethyl phosphine oxide ( $C_{10}$ DMPO) at the solution/air interface and its theoretical analysis based on the same model [4, 5].

The main equations for the frequency dependence of the visco-elasticity  $E(\omega) = E_r(\omega) + i E_i(\omega)$  are given by

$$E_r = (PR + QS)/(P^2 + Q^2), \quad E_i = [PS - QR]/(P^2 + Q^2) \quad (1)$$

and the expressions for the visco-elasticity modulus  $|E|$  and phase angle  $\phi$  between stress ( $\dot{\gamma}$ ) and strain ( $dA$ ):

$$|E| = \sqrt{(R^2 + S^2)/(P^2 + Q^2)}, \quad \phi = a \tan(E_i / E_r) \quad (2)$$

where  $P, Q, R$  and  $S$  are parameters containing the oscillation frequency  $f = 2\omega\pi$ , the thermodynamic characteristics and the diffusion coefficients of both compounds [5].

The analysis of the behaviour of mixed systems requires detailed knowledge of the single compounds. In Fig. 1 the experimental dependencies of visco-elasticity  $|E|$  and phase angle  $\phi$  on frequency  $f$  is shown for a fixed concentration of the protein. The experimental results are in good agreement with the values calculated from Eqs. (1) and (2) for the surfactant concentration  $c_s = 0$  (individual protein solution) and  $D_p = 10^{-12} \text{ m}^2/\text{s}$ . At a frequency of 0.13 Hz the visco-elasticity modulus has almost reached the limiting elasticity value while the phase angle  $\phi$  is close to zero. Note, the given diffusion coefficient  $D_p$  is much lower than expected for BLG (about  $10^{-10} \text{ m}^2/\text{s}$ ). Calculations using such large  $D_p$  values do not agree with the experimental data in Fig. 1.

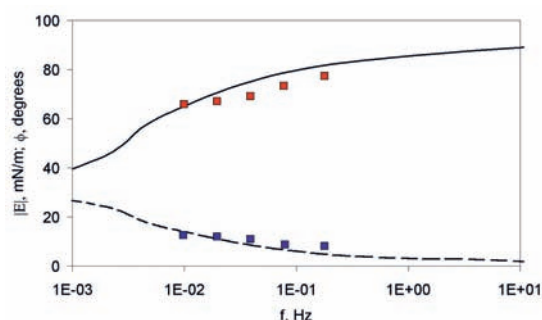


Fig. 1: Dependencies of visco-elasticity modulus  $|E|$  ( $\square$ ) and phase angle  $\phi$  ( $\blacksquare$ ) on frequency  $f$  for a  $10^{-6} \text{ mol/l}$  BLG concentration calculated from Eqs. (1) at  $c_s = 0$ ; experimental points correspond to data in [5]; the thin curves are calculations for  $D_p = 10^{-10} \text{ m}^2/\text{s}$ .

This shows that in addition to the diffusional exchange with the bulk phase other relaxation effects take place in the adsorption layer, such as molecular reformation, aggregation, etc. These processes are not analysed yet and the obtained diffusion coefficient has to be seen as an effective value.

Fig. 2 illustrates the dependence of the visco-elasticity modulus on the frequency  $f$  calculated for several  $C_{10}$ DMPO concentrations. For the theoretical dependencies the realistic surfactant diffusion coefficient of  $D_s = 3 \cdot 10^{-10} \text{ m}^2/\text{s}$  is used. The frequency increase leads to a monotonic increase of the visco-elasticity modulus  $|E|$ . However, its concentration dependence is non-monotonous with a maximum. At the same time, the dependence of  $\phi$  on  $f$  decreases monotonously, and at higher  $C_{10}$ DMPO concentration larger angles  $\phi$  are observed. The  $|E|$  values for  $C_{10}$ DMPO calculated from the theory agree satisfactorily with the experimental values (see [5]). Note, the good agreement was achieved mainly due to the assumption of an internal compressibility of  $C_{10}$ DMPO molecules in the surface layer.

The dependencies of the dilational elasticity modulus  $|E|$  on the oscillation frequency at various  $C_{10}$ DMPO concentrations in the BLG/ $C_{10}$ DMPO mixtures are shown in Fig. 3 for a fixed BLG concentration of  $10^{-6} \text{ mol/l}$ . With increasing  $C_{10}$ DMPO concentration, the elasticity modulus of the BLG/ $C_{10}$ DMPO mixture decreases significantly. For example, at 0.1 Hz the modulus for BLG mixed with 0.7 mmol/l  $C_{10}$ DMPO is 20 times lower than that for pure BLG.

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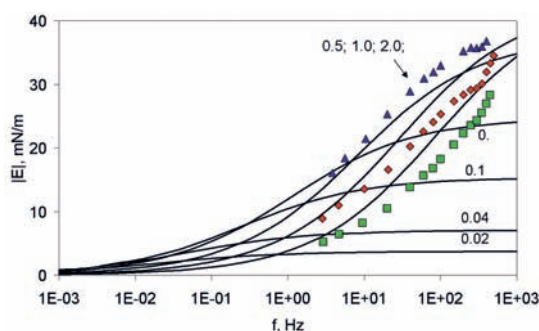


Fig. 2: Surface dilational modulus  $|E|$  versus oscillations frequency  $f$  for  $C_{10}$ DMPO solutions at various concentrations (labels refer to the concentrations given in mmol/l); experimental data for the concentrations:  $\triangle$  0.5;  $\blacklozenge$  1;  $\square$  2 mmol/l  $C_{10}$ DMPO.

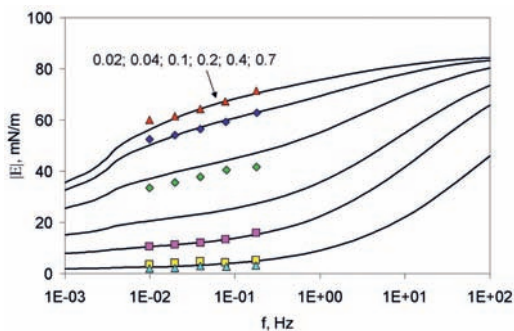


Fig. 3: Dependencies of the dilational elasticity modulus  $|E|$  on oscillation frequency  $f$  at various  $C_{10}$ DMPO concentrations (labels refer to the concentrations given in mmol/l) in the BLG/ $C_{10}$ DMPO mixtures; fixed BLG concentration of  $10^{-3}$  mmol/l and  $\blacktriangle$  0.02;  $\blacklozenge$  0.04;  $\blacklozenge$  0.1;  $\square$  0.2;  $\blacksquare$  0.4;  $\triangle$  0.7 mmol/l  $C_{10}$ DMPO.

The theoretical dependencies, also shown in **Fig. 3**, were calculated from Eqs. (1) and (2) using the respective parameters of individual BLG and  $C_{10}$ DMPO solutions as given in [5] and  $D_S = 3 \cdot 10^{-10} \text{ m}^2/\text{s}$  and  $D_P = 10^{-12} \text{ m}^2/\text{s}$ .

At  $C_{10}$ DMPO concentrations above 0.1 mmol/l the agreement becomes worse. To obtain better correspondence, one has to use (as one of the possibilities) higher diffusion coefficients for the protein, e.g.,  $D_P = (10^{-10} - 10^{-11}) \text{ m}^2/\text{s}$  instead of  $10^{-12} \text{ m}^2/\text{s}$ . Probably, in presence of a surfactant the processes of protein reformation and aggregation in the surface layer are accelerated, which increase the corresponding effective diffusion coefficient.

It should be noted that the desorption of BLG from the adsorption layer is extremely slow, and surface oscillations lead to an increase in the adsorbed amount of protein in the surface layer, while desorption of this protein during the surface compression stage can be expected to be very weak. Structural changes, i.e. formation of three-dimensional domains of BLG in the surface layer upon competitive adsorption with a surfactant and displacement of protein due to complex formation were discussed elsewhere.

The dependence of the phase angle  $\varphi$  on frequency  $f$  for the BLG/ $C_{10}$ DMPO mixture calculated from Eqs. (1) and (2) is shown in Fig. 4. For low surfactant concentrations  $\varphi$  monotonously decreases. However, with increasing  $C_{10}$ DMPO concentration a maximum in the  $\varphi$  vs  $f$  curve is observed. Note that the maximum  $\varphi$  value increases with the  $C_{10}$ DMPO concentration.

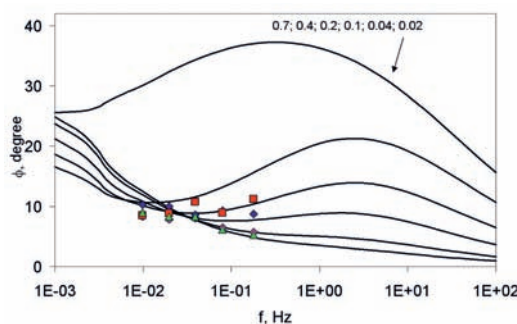


Fig. 4: Dependencies of phase angle  $\varphi$  on the oscillation frequency  $f$  at various  $C_{10}$ DMPO concentrations (labels refer to the concentrations given in mmol/l) in the BLG/ $C_{10}$ DMPO mixtures; fixed BLG concentration of  $10^{-3}$  mmol/l and  $\blacktriangle$  0.02;  $\blacklozenge$  0.04;  $\blacklozenge$  0.1;  $\square$  0.2 mmol/l  $C_{10}$ DMPO.

The last effect is attributable to the increase of the fraction of the area covered by  $C_{10}$ DMPO, because for pure  $C_{10}$ DMPO solutions in the frequency range studied a viscous behaviour was observed.

It is seen from **Fig. 4** that the experimental phase angle data agree rather well with the theoretical values calculated from Eqs. (1) and (2). For the highest  $C_{10}$ DMPO concentrations studied (0.4 and 0.7 mmol/l) the scattering of experimental data was very high (in the range of  $0^\circ$  to  $50^\circ$ ) because the visco-elasticity modulus was extremely small (2-4 mN/m, see **Fig. 3**). Therefore these data are not shown in **Fig. 4**.

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## Ion Distribution at Interfaces



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Charged surfaces are omnipresent in nature and ion-water interactions at an interface play a decisive role in various physico-chemical and biological processes. Consequently, the distribution of ions at charged interfaces defines a central theme of Colloid and Interfaces Science. Gouy and Chapman were the first who tackled this problem in a quantitative fashion. The ions were treated as point charges embedded in a continuum with given dielectric constants while the surface charge was considered to be continuously smeared out. The prevailing charge distribution generates a mean electrical potential in which the ions adopt a Boltzmann distribution. The solution of the so-called Poisson-Boltzmann (PB) equation yields the number density of the counter-ions as a function of the distance to the interface. The oversimplification of the Gouy-Chapman approach was obvious from the beginning and Stern was the first who pointed out that this theory predicts unrealistically high concentration of counter-ions in the vicinity of the interface due to a neglect of the geometrical dimensions of the ions. Since then, many extension of the theory have been put forward to account for the finite size of the ions, image forces and the dependence of the dielectric constant on the electric field or ion correlation. One striking deficiency of the treatment on the purely electrostatic level is the prediction that ions of the same valence produce the same results, independent of their chemical nature. In contrast, experiments reveal pronounced differences between different ions and any realistic theory must account for this experimental fact.

The most simple ion specific effect manifests in the surface tension of simple aqueous electrolyte solutions. In general, ions increase the surface tension in a specific manner. The effects are not dramatic; however, due to the simplicity of this system it is crucial for testing the theories. The traditional picture of the interface of an aqueous electrolyte solution is based on a thermodynamic analysis of the equilibrium surface tension iso-therm. The increase in the equilibrium surface tension is then interpreted as an interfacial zone depleted by ions. Recently this picture has been challenged by molecular dynamics simulations using polarizable force fields which predicted that soft ions such as halides are enriched at the interface with a non-monotonic ion profile [1]. The key to an understanding of this apparent contradiction lies in a reconsideration of the meaning of thermodynamics. There is no a priori prediction of a profile and thermodynamics can accommodate several conflicting interfacial models provided that the integral excess or depletion is in accordance with Gibbs equation. Therefore, direct experimental observations of molecular structure and energetics of ions in the interfacial region are required.

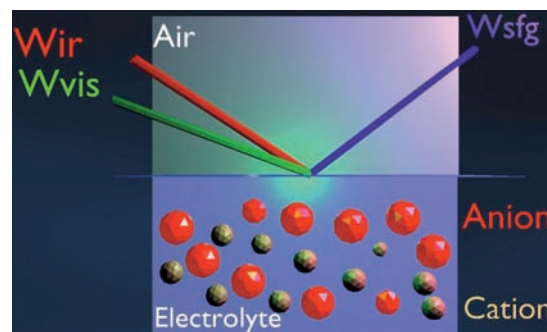


Fig. 1 Scheme of an SFG experiment: The spatial and temporal overlap of an infrared and visible laser pulse generates light at the sum frequency.

We used Infrared-Visible Sum Frequency Spectroscopy (IR-VIS SFG) to study the interfacial composition and structure of aqueous potassium thiocyanate electrolyte solutions [2]. The IR-VIS SFG spectra reveal the propensity of the thiocyanate ions at the air-electrolyte interface.

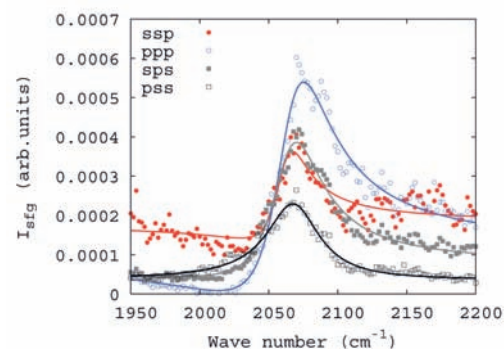


Fig. 2: Vibrational sum frequency spectra showing CN stretch of thiocyanate anion for ~1M potassium thiocyanate solution. The points and continuous lines represent the experimental data and fits respectively.

They also give access to the vibrational features of the interfacial water which are affected by the presence of the ions. Polarization dependent measurements have been used for a determination of the orientation of the pseudo-halide anion. The combined data give a picture of the interfacial architecture on a molecular scale. We believe our current study contributes towards better understanding of this biologically relevant chaotic ion and water interactions at the interface. Further our work shows that the orientation of the anion is relevant and needs to be taken into account to get a full picture on the interfacial architecture [3].



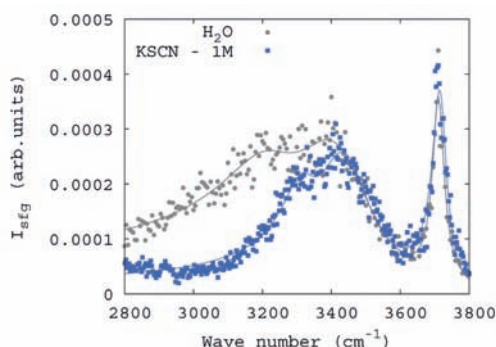


Fig.3: Vibrational sum frequency spectra of water and 1M potassium thiocyanate solution. The points and continuous lines represent the experimental data and fits, respectively.

### Surface Rheology

Surface rheology governs a great variety of inter-facial phenomena such as foams or emulsions and plays a dominant role in several technological processes such as high speed coating [5]. Its major difference with bulk rheology resides in the high compressibility of the surface phase, which is the direct consequence of the molecular exchange between adsorbed and dissolved species. In analogy to bulk rheology, a complex surface dilational modulus,  $\epsilon$ , that captures surface tension changes upon defined area changes of the surface layer, can be defined. The module  $\epsilon$  is complex and the molecular interpretation of the dissipative process that gives rise to the imaginary part of the module is subject to some controversy. We used the oscillating bubble technique to study the surface dilational modulus in the mid-frequency range [6]. The dynamic state of the surface layer was monitored by a pressure sensor and by surface second harmonic generation (SHG). The pressure sensor measures the real and imaginary part of the modulus while SHG monitors independently the surface composition under dynamic conditions. The experiment allows the assessment of the contribution of the compositional term to the surface dilational modulus  $\epsilon$ . Two aqueous surfactant solutions have been characterized; a surface elastic and a surface viscoelastic solution.

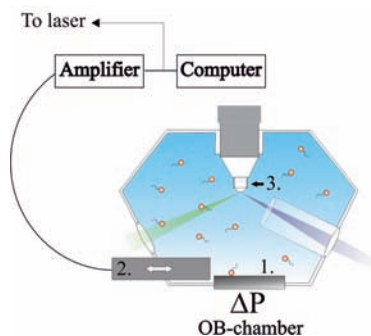


Fig. 4: Cross sectional view of the oscillating bubble device. The piezo translator is immersed in the liquid, the bubble is formed at the tip of the capillary and the pressure is recorded by a sensitive pressure transducer at the bottom of the chamber. The piezo movement leads to an expansion and compression of the surface layer. The surface state can also be probed by Second harmonic generation in total reflection mode.

The elastic surface layer can be described within the framework of the extended Lucassen-van den Tempel model. The change in surface concentration is in phase with the relative area change of the surface layer, which is in strong contrast with the results obtained from the surface viscoelastic solution. Here surface tension, area change and surface composition are phase shifted providing evidence for a nonequilibrium state within the surface phase. The data are used to assess existing surface rheology models [7].

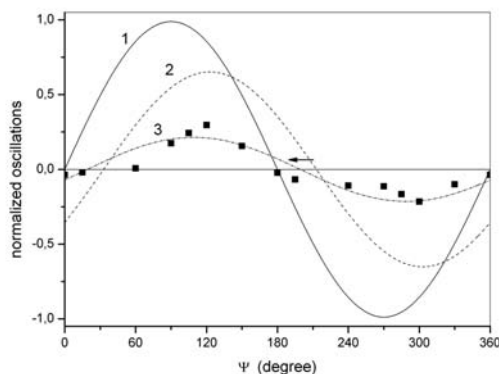


Fig. 5: Dynamic characteristics of surfaces of 4mM DMPB solutions as function of the phase angle. The solid line represents the normalized area change, the dashed line represents the normalized change in dynamic surface tension and the square dots are the changes in the surface coverage measured by SHG

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## SOLID INTERFACES

# Nucleation, Interfacial Molecular Mobility and Ordering of Alkanes at Solid/Vapor Interfaces



Long chain *n*-alkanes at solid/air interfaces serve as model system to investigate two-dimensional nucleation, solidification, structure formation, and wetting properties of molecularly thin organic layers.

Our research focuses on the interaction/coupling between solid/liquid phase transitions and molecular transport (wetting, molecular flow, etc.). In fundamental science these processes are important in the early stages of solidification/melting (nucleation, cluster formation) as well as (non-equilibrium) bulk aggregation. In applied science our research is relevant for 2-dimensional systems or systems with small dimensions, e.g. microfluidics, nanotechnology, etc.

We specifically address the following topics/questions: What processes govern two-dimensional nucleation for different surface coverages and cooling rates? What is the relation between the interfacial alkane ordering and the statics and dynamics of wetting? Into which domain morphologies aggregate the interfacial molecules under various growth conditions?

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on planar solid surfaces

Molecularly thin films of long chain *n*-alkanes at solid/gas interfaces show an amazing variety of different topologies (droplets, domains, films, layers, terraces, ...) depending on the surface coverage, temperature, and preparation history. For instance, C<sub>30</sub>H<sub>62</sub> at SiO<sub>2</sub>/air-interfaces shows three temperature regions of distinctly different topologies (**Fig. 1**):

- 1.) At  $T > T_{sf}$  ( $sf =$  "surface freezing") all alkane is molten. It forms a completely wetting film of uniform thickness.
- 2.) In an intermediate range (**Fig. 1**: medium blue background), the alkane adjacent to the solid surface solidifies ("surface freezing"). If there is excess alkane ("excess coverage"), it remains liquid and shows a wetting transition at  $T_{sf}$  from a completely wetting film to droplets on top of the frozen layer. In the case of "submonolayer coverage", solid domains coexist with liquid (mobile) alkane in between.
- 3.) Below the bulk melting temperature,  $T_{bulk}$ , in case of excess coverage, the alkane solidifies into multilayers (terraces).

### Excess Coverage:

The melting behaviour of the solid multilayers is quite peculiar. At  $T_{bulk} < T < T_{sf}$  the melting alkane forms droplets which move [3]: They "eat" into the solid terraces while increasing their volume (**Fig. 2**). These "running droplets" are a consequence of mass conservation and autophobicity (the molten alkane forms nonwetting alkane droplets on top of the surface frozen monolayer).

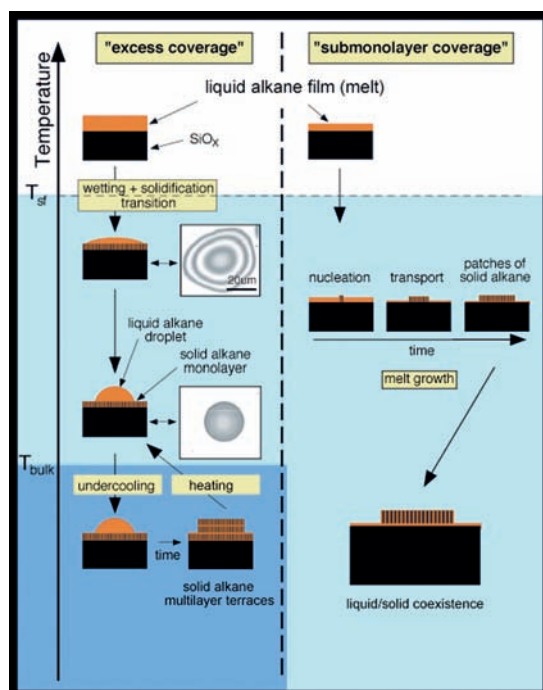


Fig. 1: Various alkane topologies in the case of "excess" coverage (=overall coverage exceeds one molecular length) and "submonolayer" coverage.

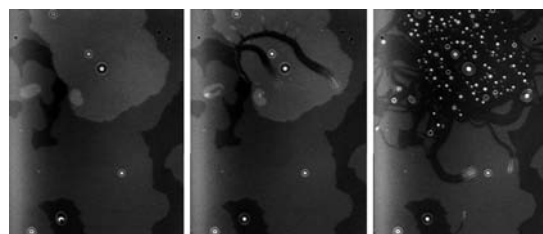


Fig. 2: Droplets of C<sub>30</sub>H<sub>74</sub> moving into bilayers (bright grey) and monolayers (medium grey) on top of the surface frozen monolayer (dark grey background). From left to right the temperature was increased continuously (stroboscopic illumination: 10 flashes/frame; area:  $\approx 70\mu\text{m} \times 50\mu\text{m}$ ).

The droplet speeds are determined by the balance between capillary and friction forces with the melting enthalpy as energy source (**Fig. 3**).

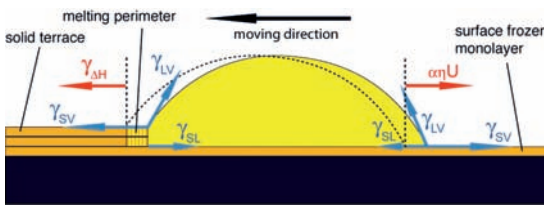


Fig. 3: Forces and energy balance of the moving droplets

Fig. 4 shows the speeds as function of temperature and terrace heights in agreement with the model of Fig. 3 [3].

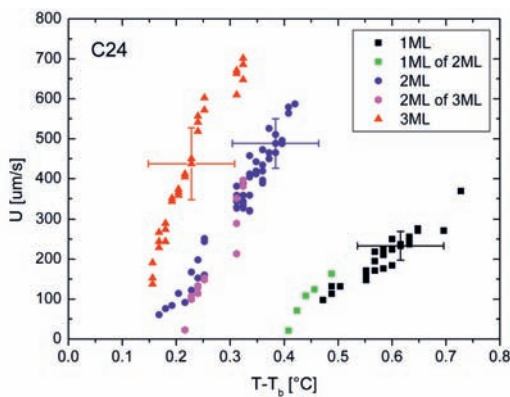


Fig. 4: Velocity vs. temperature for droplets melting into monolayers (1ML), bilayers (2ML), and three melting layers (3ML) of  $C_{24}H_{50}$  directly on top of the surface frozen layer. ( $T_b$ =bulk melting temperature).

### Submonolayer Coverage:

Optical imaging with molecular depth resolution [4] allows the online investigation of nucleation and growth of solid, fractal domains (Figs. 4 and 5) on the  $SiO_2$ /air-interface.

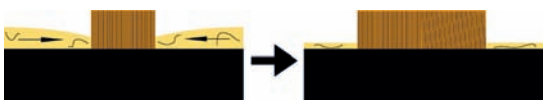


Fig. 5: Submonolayer coverage: Domain growth and alkane flow (arrows) with depletion zone next to the domains.

Depletion zones (Fig. 6, darker areas) reveal details on the lateral flow/transport processes in molecularly thin films.

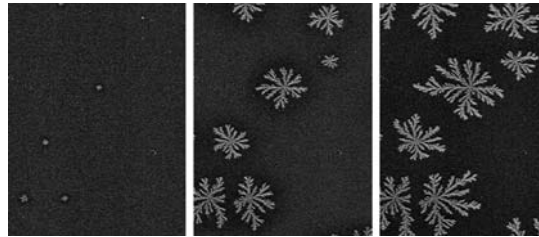


Fig. 6: Submonolayer coverage: Growth of solid alkane domains upon cooling. Frame size  $\approx 0.6\text{mm} \times 1\text{mm}$  [4].

A quantitative analysis of the domain size as function of the temperature as well measurements of the alkane coverage in between the solid domains reveals the equilibrium coexistence of solid and liquid alkane over a wide temperature range (Fig. 7). This is explained by the contribution of the thickness-dependent interfacial potential to the chemical potential of the alkanes, which leads to a thickness-dependent melting point [5].

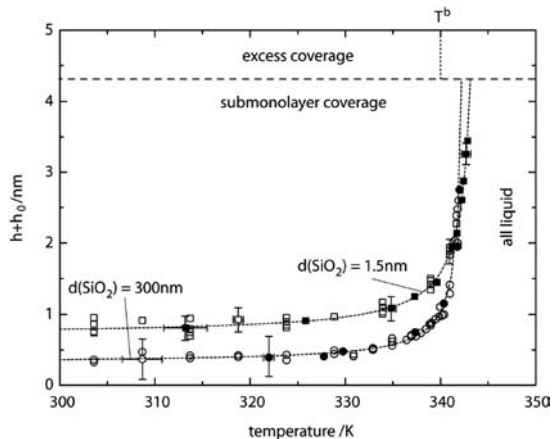


Fig. 7: Phase transition temperatures as function of the thickness of the liquid film in between the domains for substrates with thin ( $\approx 1.5\text{nm}$ , squares) and thick ( $\approx 300\text{nm}$ , circles)  $SiO_2$ -layers.

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### References:

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## NON-PLANAR INTERFACES

# Nanoscale Membranes: Narrowing the Gap between Materials Science and Biology



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Thesis: Measurement of sedimentation velocity of colloids

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From Method-development to Understanding Structure-property Relations

**Since 2007:** Professor

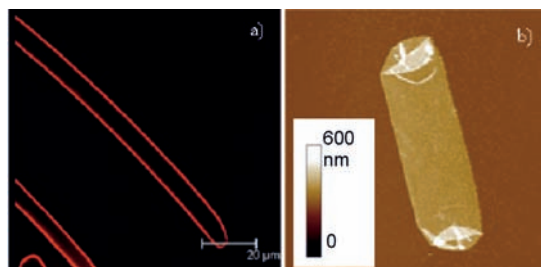
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Membranes with nanoscale thickness are abundant in nature, for example in form of the walls of cells, viruses or bacteria. These examples show impressively that membranes can be more than just static “barriers”: Rather they can be sensitive towards external parameters like stress or chemical environment, adapt to their environment or carry out active processes like movement. Artificial mem-

branes are far from being so “smart”, but in recent years tremendous progress has been made in their production and a major goal is to narrow the gap between these two worlds. In the past two years, we have focused on developing tools for studying mechanical properties in membrane systems, investigating and designing stimuli responsive nanoscale membranes and have taken first steps towards understanding biomimetic motion on colloidal scale and transferring it to artificial systems.

Our main tool for investigating mechanics of membranes is the atomic force microscope (AFM). Using AFM, nanoscale deformations can be applied and a force range between 10s of piko-N up to a micro-N is accessible. During the past years we have applied colloidal probe AFM in combination with optical techniques for studying the force-deformation characteristics of individual (hollow) microcapsules and developed continuum and finite element analysis methods to derive elastic constants of the membrane materials from the measurements. While originally we were mainly focusing on micron sized microcapsules, we have recently expanded this approach to submicron objects like unilamellar small vesicles [1]. As well, we have developed (mostly AFM-based-) techniques for quantifying elastic constants for other membrane geometries like tubes [2] (Fig. 1 displays an example of polymeric tubes made from nanoscale polymeric membranes) or flat membranes. Thus the versatility of the method could be greatly improved.

Going beyond static experiments on mechanical properties, we have explored stimulus sensitivity of polyelectrolyte multilayers in depth. We could for the first time show, that certain polyelectrolyte



*Fig. 1: Microtubes (confocal microscopy image on left hand side with nanoscale membranes as walls (right hand side displays AFM image of a collapsed tube from which the membrane thickness can be derived. Elastic constants can be derived from AFM-based force spectroscopy experiments.*

multilayers exhibit a transition from a glassy material to a viscoelastic fluid upon temperature increase in aqueous environment [3]. The glass transition of the multilayer material results in greatly increased deformability as shown in Fig. 2 and can explain earlier observed shape changes of microcapsules upon heating as surface tension effects. Like on the macroscale, where the success of polymeric materials is largely due to the fact that they can be formed easily at temperatures above their glass transition temperature while being highly form stable below it, this opens new perspectives for shaping nanoscale membranes.

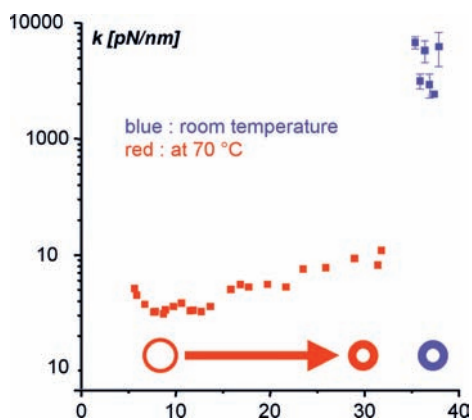


Fig. 2: The stiffness  $k$  (slope of the force-deformation characteristic) of an individual microcapsule monitored when first heating and then suddenly cooling the capsule from 70 degrees C to room temperature (semi-logarithmic scale). While at high temperature capsule stiffness gradually increases due to shape changes of the capsule, quenching results in a two orders of magnitude stiffening due to an increase in the material's Young's modulus [3].

While glass transitions are common in polymeric materials, polyelectrolyte multilayers offer alternate possibilities for triggering changes in deformability due to the charge they carry. pH changes can cause charge imbalance and lead to strong capsule swelling due to internal electrical fields. For cross-linked membranes these shape changes are reversible and we could demonstrate that they are accompanied by deformability changes over orders of magnitude [4], offering yet another pathway towards stimuli responsive membrane systems.

One stunning feature of biological microcapsules like bacterial capsids is their ability to move actively and generate forces. We have started studying the mechanisms underlying bacterial movement by investigating in vitro systems [5]. In particular, we have focused on the case of motion based on actin gel polymerization/depolymerization like it is employed by listeria monocytes. This mechanism can be well transferred to colloidal particles which are coated by proteins and exposed to suitable solutions. The colloidal particles can – in contrast to their bacterial counterparts – be well controlled in shape and offer thus new possibilities to shed light on the movement process. Fig. 3 shows a snapshot of colloidal particles actively moving in micro-channels. 3

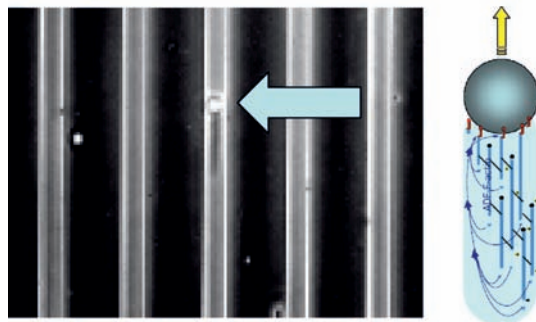


Fig. 3: On the left-hand side, a snapshot of a colloidal particle moving up a microchannel by means of actin polymerization / depolymerization is displayed. Behind the particle (marked with the arrow), a dark cone of actin gel is clearly visible, which is pushing the particle upwards. On the right hand side, a schematic (courtesy M.F. Carlier, Univ. Paris XI) of the underlying actin polymerization / depolymerization process is displayed.

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## From Molecular Modules to Modular Materials



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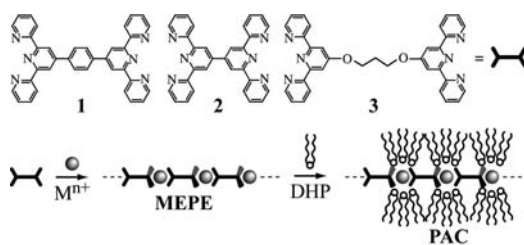
Thesis: Self-Assembly of Hierarchically  
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Weak competing interactions provide an efficient and elegant route to self-assemble supramolecular materials with a wide range of value-adding and dynamic properties. Metal ion induced self-assembly is one of the major recognition motives in supramolecular chemistry. The resulting metallo-supramolecular modules possess structural, kinetic, magnetic, optic, electronic, and reactive properties that are relevant for functional devices and materials of technological interest.

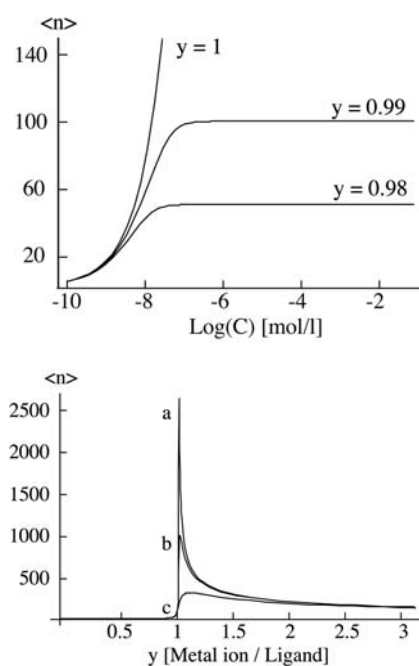
Materials built up through weak interactions can assemble, disassemble and reconstruct in a dynamic fashion under ambient conditions. Such materials can be adaptive and responsive. Structure and property are dynamic, that is, they depend on external parameters, such as temperature, pH, solvent, ionic strength or external fields, and in addition such materials have the ability to self-repair, self-anneal and self-correct under ambient conditions.

While polymers based on kinetically inert transition-metal complexes are readily characterized in solution by standard analytical means, polymeric assemblies formed by kinetically labile transition-metal complexes have successfully evaded characterization. Due to the enormous prospects of dynamic polymers, we have taken a detailed look at the formation, self-assembly, structure and properties of dynamic macromolecular assemblies using ditopic bis-terpyridine ligands, e. g. 1,4 bis(2,2':6',2''-terpyridine-4'-yl)benzene and kinetically labile transition metal ions including Fe, Co, Ni, and Zn. A high binding affinity and a well-defined stereochemistry make these building blocks attractive components for the assembly of dynamic and functional metallo-supramolecular coordination polyelectrolytes (MEPEs) (**Scheme 1**) [1]. The availability of processable MEPEs has stimulated research concerning composite nanostructures [2], Langmuir and Langmuir-Blodgett [3] layers, thin films, capsules, and liquid crystals [4], electrochromic windows [5], and magnetic materials [6].



**Scheme 1:** Metal-ion induced self-assembly of ditopic bis-terpyridines such as 1, 2, and 3, results in metallo-supramolecular coordination polyelectrolytes (MEPEs). Sequential self-assembly with amphiphiles such as dihexadecyl-phosphate (DHP) results in the corresponding polyelectrolyte-amphiphile complexes (PAC).

In a first approximation, the mean molar mass depends on the concentrations and the stoichiometry of the constituents and is determined by the dynamic equilibrium of association and dissociation. On increasing the concentration, the mean length is shifted to larger assemblies. The theory of self-assembly predicts an exponential growth as a function of concentration. If the stoichiometry of the two constituents, that is the ratio of metal ions to ligands, deviates from one, the length of the aggregates is finite. Above a certain concentration, the length of the aggregates reaches a threshold value and becomes independent of concentration. Based on fundamental principles of thermodynamics we calculated the molar mass (**Fig. 1**). Notably, there is a strong non-linearity for the molar mass at a given concentration in the vicinity of the stoichiometric ratio  $y=1$ , which is interesting for technological uses including adhesion and power transmission. Qualitatively, these findings were confirmed by viscosity measurements and molar mass determination using analytical ultracentrifugation. Not surprisingly we also find that MEPE solutions are thixotropic, another property of technological interest.



**Fig. 1:** Average number of monomers per assembly  $\langle n \rangle$  as a function of concentration,  $C$ , (top) for different stoichiometries  $y$ , and as a function of stoichiometry,  $y$ , (bottom) for different monomer concentrations ( $a$ :  $10^{-3}$  mol/L,  $b$ :  $10^{-4}$  mol/L,  $c$ :  $10^{-5}$  mol/L). Here, the stability constants of Fe(III) and terpyridine are used).

The dynamic nature effectively prevents the formation of crystals suitable for structure analysis. Essentially, there is no structural information on the molecular level available for these materials. We were able to grow nanoscopic crystals on surfaces and we were successful in structure determination by electron diffraction. [7] The occurrence of metal ions in MEPEs is a fortunate coincidence because they enhance



contrast for diffraction. We have chosen Fe(II) as central metal ion in order to use Mössbauer spectroscopy as complementary tool to probe the coordination environment of the metal complexes. Similar to protein crystallography, we have used a combination of diffraction data and molecular modeling to refine the structure to near atomic resolution. The analysis by electron diffraction reveals a primitive monoclinic unit cell, in which the MEPE forms linear rods, which are organized into sheets (Fig. 2). Four sheets intersect the unit cell, while adjacent sheets are rotated by 90° with respect to each other. Mössbauer spectroscopy of bulk samples confirms the pseudo-octahedral coordination geometry and indicates an average length of approximately 8 repeat units in the solid state.

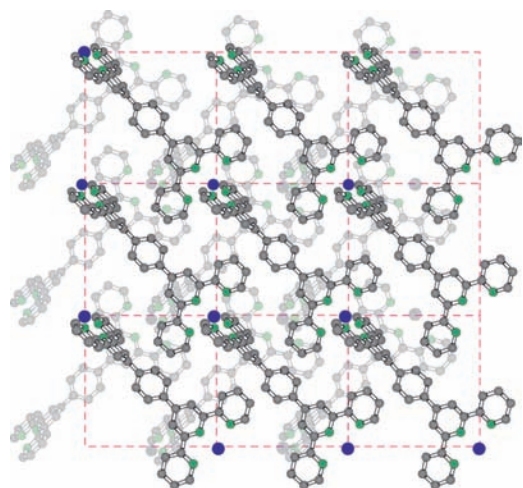


Fig. 2: Structure of MEPE based on FeOAc<sub>2</sub> and 1. The MEPE forms linear rods that are organized into sheets. The unit cell consists of four sheets, while each sheet is rotated by 90° with respect to each other. The coordination geometry is pseudo-octahedral.

A route towards mesophases of metallo-supramolecular polyelectrolytes is based on the exchange of the counter ions by suitably charged amphiphilic molecules. Amphiphilic self-assembly of MEPE and negatively charged surfactants such as dehexadecyl phosphate (DHP) affords the corresponding polyelectrolyte-amphiphile complex (PAC) (Scheme 1). The combination of rigid-rod polymers and flexible surfactants gives rise to polymorphism. A combination of X-ray scattering and molecular modeling was used to reveal details of the architecture. Notably, DHP forms an interdigitated layer in this structure in contrast to the solid-state structure of DHP and the typical packing motives encountered in amphiphilic architectures. [8] The PAC structure is a nice example of a multi-component hierarchical architecture: At the molecular level the structure is determined by the design of the ligands and the metal coordination algorithm. At the mesoscopic length scale structure arises through the interaction of the MEPE rods and the amphiphilic molecules. And finally at the macroscopic level, structure arises through the packing of the PAC rods into the final architecture.

The phase transition in the amphiphilic mesophase is explored to deliberately induce mechanical strain in an assembly of the tightly coupled metal ions in MEPES. Melting of the alkyl chains in the amphiphilic mesophase induces mechanical strain thus in turn distorting the coordination geometry around the central metal ions. As a result, the crystal field splitting of the d-orbital subsets decreases resulting in a spin transition from a low-spin to a high-spin state. The diamagnetic-paramagnetic transition is reversible. Liquid crystalline materials are readily processed into various device architectures, and the concept can be expanded to virtually all metallo-supramolecules polymers with suitable electronic configurations. [9]

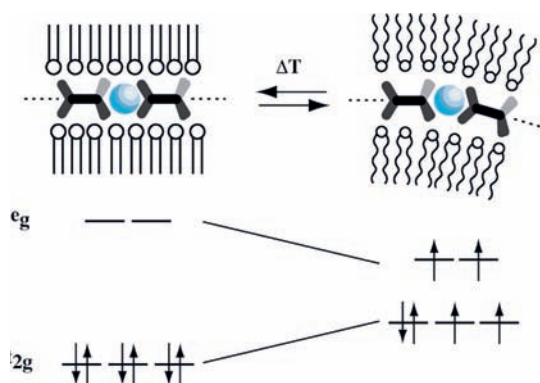


Fig. 3: Melting of DHP in PAC results in a distortion of the coordination geometry (top), giving rise to a reversible spin transition from a low- to a high-spin state (bottom).

Carrying metal ions into macromolecular assemblies may provide a strong impact on polymer chemistry and materials science. It is safe to predict that in the future polymer research will exploit the elements of the entire Periodic Table in systematic ways as weak or strong chain or network forming units. The extension of macromolecular chemistry beyond carbon-based polymers offers unlimited structural possibilities and provides an enormous potential to improve the capacity of macromolecular materials with many new dynamic, thermal, electronic, electrical, photo-electrical, static, mechanical etc. properties [9].

Other areas of interest include structure-property relationships in functional materials based on polyoxometalate clusters [10] and fullerenes [11].

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## Biomimetic Vectorial Electron Transfer



## Aims

Vectorial electron transfer across a membrane leads in nature to a potential and/or chemical difference of the two separated compartments, e.g. in photosynthesis or in the respiratory chain. This finally leads to products which store energy or information. Mimicking this process in artificial systems may lead to new types of energy converters or sensors.

For most efficient directed electron transfer on one hand the energy levels of donor and acceptor have to be suited (downhill transfer) on the other hand the relative arrangement of the participating groups has to be adapted to maximize a transfer integral. Nature generally uses only one type of chromophore, porphyrin derivatives, (chlorophyll, pheophytin, Fe – containing porphyrins) and optimizes energy levels and orbital overlap by changing the local environment and fixing the groups within a protein matrix. On a much more primitive level we replaced the protein matrix and the lipid membrane by a polyelectrolyte multilayer. Into this we incorporated in project A pyrenes as chromophores with well – known photophysics. Building a film with a polarity gradient by consecutive adsorption of different polyelectrolytes we thus expect that photoinduced electron transfer should occur into only one direction (Fig. 1). In project B we incorporate cytochrome c (cyt c) as a well – known electron transfer protein into the film and ask on the influence of the matrix on the electron transfer between protein and electrode as well as between different cyt c.

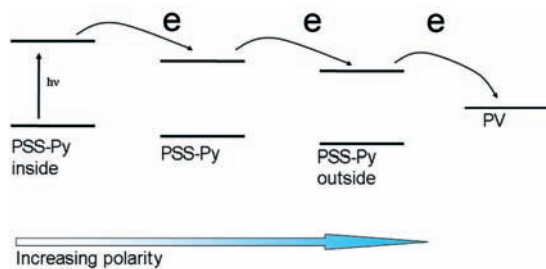


Fig. 1: In this work PSS – Py has been replaced by polyacrylic acid with 3mole% grafted pyrene (PAA – Py)

## Results

## A – Electron Transfer between Pyrenes

In previous work we have shown that photoinduced electron transfer across the film occurs quantitatively if the average distance between the chromophores is below 3.0 nm, i.e. even in absence of orbital overlap. This surprising result raises the question if the conjugated bond in polystyrenesulfonic acid facilitates the transport by mixing with donor and acceptor orbitals. This so called superexchange mechanism could now be ruled out by building up a film with the only conjugated bonds being those of the chromophore. Fig. 2 shows that the pyrene fluorescence can be almost completely quenched by adding a polymeric acceptor (PV) that cannot penetrate the film [1].

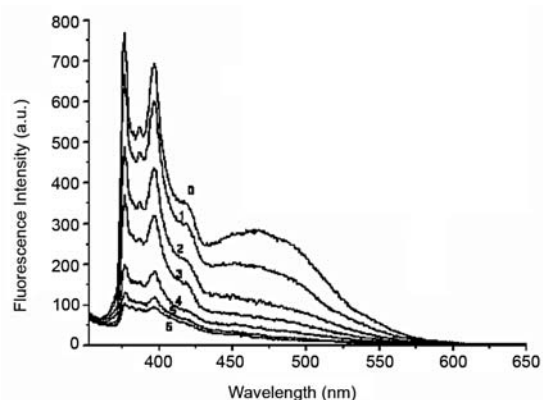


Fig. 2: Fluorescence spectra of multilayers composed of 4 bilayers of PAA – Py and polyallylaminhydrochloride (PAH) at increasing concentrations of polyviologen from 0-6

- The above result can only be understood if the lifetime of the pyrene anion and/or cation is sufficiently large to enable long – range electron transfer. Indeed in collaboration with the group of R. Menzel (University Potsdam) we could show by time resolved absorption spectroscopy that the lifetime of these ions exceeds 10 µsec, and is even further increased in case of a polarity gradient. [2]
- In photopotential measurements with multilayers it was also shown that the lifetime of charge carriers and hence the potential can be drastically increased by going from a symmetric to an asymmetric film (Fig. 3, [3]). For the symmetric film switching on and off illumination the photovoltage changes by 4 mV within less than 2 min, whereas for the film with polarity gradient the change is more than an order of magnitude larger, and on switching off the light the photovoltage decay takes more than 30 minutes. This indicates that also charges that have relaxed into deep traps are released at times depending on the local environment.

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1974-1975: Postdoc (IBM San Jose)

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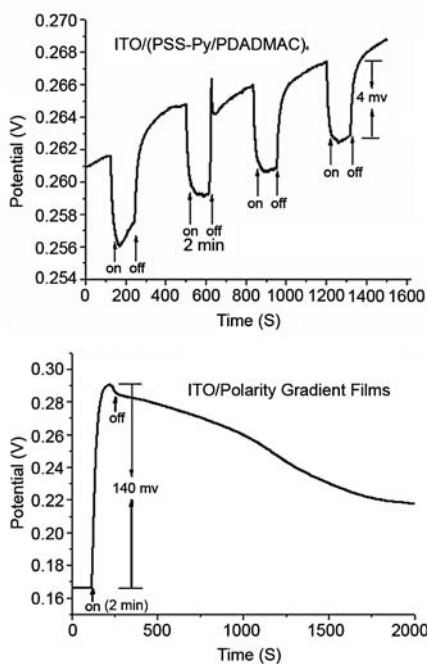


Fig. 3: Photopotential of a polyelectrolyte film containing PSS – Py before and after illumination at 355 nm measured between 0.1 M KCl solutions and an ITO electrode. Fig. 3a: 4 bilayers of PSS – Py and Polydiallyldimethylammonium chloride (PDADMAC). Fig. 3b: polarity gradient film existing of 4 bilayers of PSS – Py/ PDADMAC followed by 4 bilayers of PSS – Py/ PAH and then PSS – Py/ polyethylenimine.

### B – Electron Transfer Involving Cyt c

- In collaboration with the group of P. Hildebrand (TU Berlin) the electron transfer between cyt c and rough Ag electrodes was studied by surface enhanced resonance Raman spectroscopy. It was shown that depositing the cyt c on a defined polyelectrolyte film causes a mixing, and hence the desired layered geometry is lost [4]. It is also shown that the polyelectrolyte environment influences the detailed mechanism of the electron transfer process. The intermixing may be caused by the rough support necessary to apply this technique.

- In collaboration with the group of F. Scheller (University Potsdam) we have previously shown by cyclic voltammetry that not only cyt c near the electrode but also that within a 10nm thick film contributes to the electron transfer [5]. The initial aim was to achieve this by connecting the cyt c via conducting polymers inserted into the film. However, it turned out that this is not necessary, because the cyt c appears to assume proper relative orientation to enable efficient electron transport. This principle has recently been extended to prepare an efficient electron transfer chain with cyt c being a mediator between a redox enzyme and an electrode. (Fig. 4, [6]) This may become a new concept for biosensors because coupling different enzymes, again in analogy to nature, enhances the specificity, and having more partners in the film than in a monolayer enhances the sensitivity.

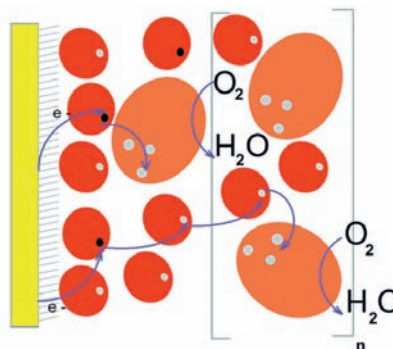


Fig. 4: Representation of the redox reaction chain at cytochrome c/bilirubin oxidase (cyt.c/BOD) electrodes. Red circles = cyt.c molecules, ellipses = BOD molecules, arrows indicate electron transfer pathways between cyt.c and BOD within the polyelectrolyte network to enable four-electron oxygen reduction process.

### Future Work

Project A has been terminated, but similar experiments are planned with porphyrines and their aggregates in polyelectrolyte films. This would bring the system closer to biology and also enable Resonance Raman spectroscopy. In addition other gradients will be prepared by incorporating also asymmetric lipid bilayers in cooperation with the group of R. Krastev.

In project B the quantitative coupling of different enzymes and thus of reactions appear most promising. Raman spectroscopy has been shown to be a most suitable tool to study the electron transfer mechanisms. However, the need of rough Ag electrodes is very problematic because of their influence on film structure. Therefore in order to avoid the artefacts we intend to deposit Ag or Au nanoparticles on the film to achieve the plasmon enhancement and thus to be able to use smooth supports.

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## NON-PLANAR INTERFACES

# Active Coatings Based on Incorporated Nanocontainers (Nanofuture Group)



Development of a new generation of multifunctional coatings, which will possess not only passive functionality but also active and rapid feedback activity in response to changes in local environment, is a key technology for fabrication of future high-tech products and functional surfaces [1,2]. These new multifunctional coatings should combine

passive components inherited from "classical" coatings (barrier layers) and active components, which provide fast response of the coating properties to changes occurring either in the passive matrix of multifunctional coatings (e.g., cracks, local pH change) or in the local environment surrounding the coating (temperature, humidity) (Fig. 1). The coatings should also have several functionalities (e.g., antifriction, antifungal, and anticorrosion) exhibiting synergistic effects.

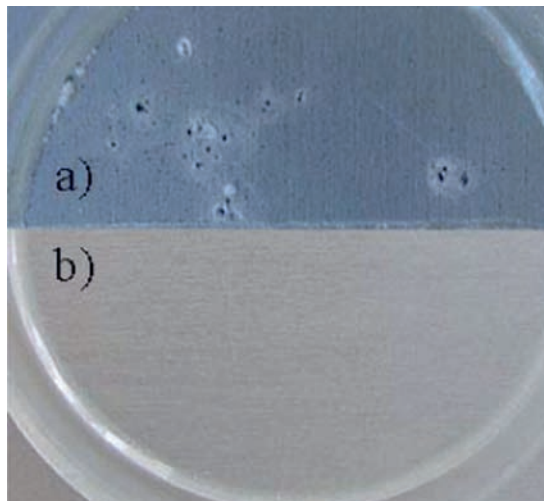


Fig. 1.: Aluminium substrate coated with  $ZrO_2/SiO_2$  sol-gel film after 14 days in 0.005 M NaCl (a) and  $ZrO_2/SiO_2$  sol-gel film impregnated with benzotriazole-loaded  $SiO_2$  nanocontainers after 14 days in 0.5 M NaCl (b)

The most important part in the design of new active coatings is to develop nanocontainers with good compatibility to the matrix components, possibility to encapsulate and upkeep active material and permeability properties of the shell controlled by external stimuli. The nanocontainers should also be of a size less than 300-400 nm. The nanocontainers of larger size can damage the integrity of the coating matrix forming large hollow cavities, which reduce the passive protective properties of the coating. Depending on the nature of the sensitive components (e.g., weak polyelectrolytes, metal nanoparticles) introduced into the container shell, reversible and irreversible changes of the shell permeability can be induced by various stimuli: variation of the pH, ionic strength, temperature, ultrasonic treatment, alternating magnetic field, electromagnetic fields. Different responses of the container shell can be then observed varying from fine effects like tuneable permeability to more drastic ones like total rupture of the container shell.

Perspective nanocontainers can be divided into two families regarding their mechanical properties and compatibility with the passive matrix of the coating: (i) organic nanocontainers for organic films and (ii) inorganic or composite nanocontainers for mostly oxide-based sol-gel or metal coatings. Most promising nanocontainers (considering their shell stability and versatility of the shell modification) can be fabricated by three general approaches. The first one is based on self-assembly of amphiphilic block copolymers into spherically closed nanostructures followed by cross-linking to stabilize the nanocontainer shell. The second procedure comprises layer-by-layer assembly of oppositely charged species on the outermost surface of dense template nanoparticles using polyelectrolytes, conductive polymers, biopolymers, carbon nanotubes, viruses, lipid vesicles, and nanoparticles as constituents of the nanocontainer shell. The third approach involves the use of ultrasonic waves to fabricate inorganic and composite hollow nanospheres. In this case, a cavitation microbubble is employed as a template on whose surface an inorganic shell is formed from precursors or pre-formed nanoparticles adsorbed at the gas/liquid interface.

Self-organizing block copolymer nanocontainers provide the possibility of entrapping hydrophobic inhibitors, oils or bioactive materials in the core making them dispersed in water. The sizes of nanocontainers can be varied from nanometres to hundreds of nanometres by changing the molecular weight of the polymer and the ratio between the block sizes. The polymer shell can be stabilized by cross-linking or electrostatic deposition of polyelectrolytes and nanoparticles.

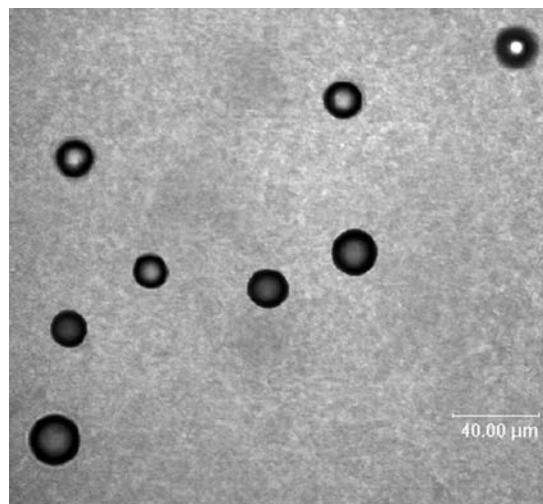


Fig. 2: Confocal microscopy images of the air-filled nanostructured silica spheres made in bright field mode. Silica shell has quartz crystal phase.

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Another type of functional nanocontainers can be fabricated by Layer-by-Layer assembly of oppositely charged species [3]. The universal character of the method does not have any restriction on the type of the charged species employed for shell construction. The precision of one adsorbed layer thickness is about 1 nm. The shell of the polyelectrolyte nanocontainers is sensitive to a variety of physical and chemical conditions of the surrounding media (pH, ionic strength, irradiation, magnetic field, etc.).

Fabrication of inorganic nanocontainers was demonstrated using the interface of the cavitation bubble as a template [4]. Hollow inorganic spheres can be formed by either ultrasonically induced reactions between initial precursors (e.g., salts) at the gas/liquid interface of the cavitation bubble or by melting (or sonoinduced welding) and condensation of the as-prepared and surface-modified nanoparticles at this interface (Fig. 2). Acoustic cavitation appears in the liquids at high and moderate intensities of ultrasonic irradiation. The minimum power intensity required for ultrasonic cavitation increases with increase of the frequency of ultrasound. The liquid expands during the expansion by the sound field ("negative pressure"). This results in rapid growth of the weak sites of the liquid predominantly containing dissolved gases ("cavitation nuclei") thus producing vapor and gas-filled cavities or microbubbles. Then, the liquid compresses during the compression phase of the sound field ("positive pressure"). The bubbles continue to grow during the negative/positive cycles until reaching a critical diameter, which depends on ultrasound frequency and nature of the liquid.

The collapse of the critical cavitation microbubble in liquids results in an enormous concentration of energy from the conversion of the surface energy and kinetic energy of the liquid motion into heat or chemical energy. The high local temperatures (5000-7000 K inside a cavitation bubble) and pressures combined with rapid cooling provide unique means for forming nanocontainers with non-equilibrium structure under extreme conditions. The characteristics of the shell of ultrasonically produced nanocontainers can be changed by decorating it with suitable hydrophilic and hydrophobic organic moieties.

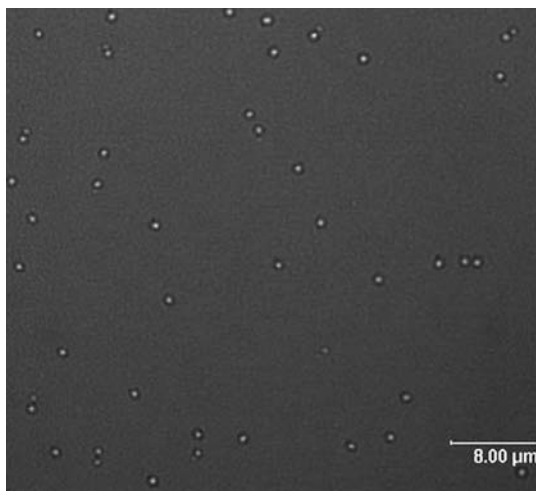


Fig. 3: Confocal microscopy images of toluene-loaded polyglutamate/polyethylene imine/polyacrylate containers in aqueous phase in bright field mode. Average diameter of the containers is 600 nm.

An approach for facile entrapment of the hydrophobic active materials inside polyelectrolyte nanocontainers dispersed in water phase was developed combining ultrasonic technique and Layer-by-Layer assembly protocol. Polyglutamate/polyethyleneimine/polyacrylate nanocontainers loaded with the hydrophobic dye 5,10,15,20-tetraphenylporphyrin dissolved in toluene were fabricated (Fig. 3). About 600 nm in diameter, uniform, stable and monodisperse nanocontainers were obtained. The hydrophobic core of the nanocontainer might contain a big variety of water-insoluble active materials (e.g., drugs, corrosion inhibitors, lubricants) and the outer polyelectrolyte shell has controlled permeability and desired multifunctionality and enables dispersion of the inner hydrophobic content in hydrophilic environment. Addition of the surface-active material (sodium dodecyl sulfate) on the ultrasonic preparation stage leads to a 10-fold increase of the amount of nanocontainers, their monodispersity and stability. Surface active material sharply decreases the surface tension at the interface of the cavitation microbubble prolonging its lifetime thus allowing more dissolved polyglutamate molecules to be condensed at the cavitation interface.

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## Multifunctional Polymer Micro-Capsules



Polyelectrolyte multilayer capsules continuously attract interest due to a number of fundamental and applied aspects of research. In last years we studied temperature and pH behavior of capsules, guiding permeability and optical addressing to capsule properties as well as were aiming to deliver the capsules to cells and monitoring capsule in living cells.

The temperature-dependent behavior of polyelectrolyte multilayer microcapsules in aqueous environment was investigated from the fundamental point of view, but also with respect to possible applications. To obtain reliable results of pure multilayers, silica particles were introduced as routine templates for capsule preparation and the coating as well as the core dissolution process was optimized for each system used. As studied by a variety of physical methods the influence of different parameters, e.g. type of the used polyelectrolytes, layer number, sequence of layering, charge balance, molecular weight of the polyions, capsule size, cross-linking, and degree of aggregation on the thermal response of capsules were found to have tremendous influence on temperature behavior of capsules (**Fig. 1**) [1].

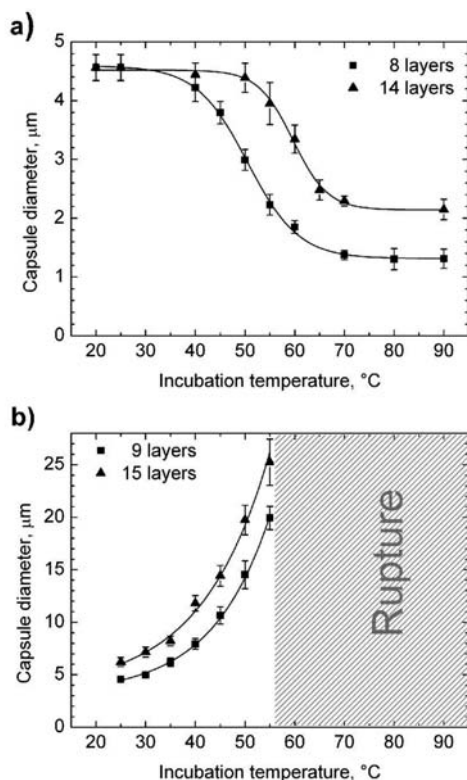


Fig. 1: Quantification of the shrinkage and swelling of PDADMAC/PSS capsules with even (a) and odd (b) layer numbers.

Differential scanning calorimetry measurements of capsules revealed that multilayers undergo a glass transition in water, at which the polymer material softens allowing rearrangements to occur. The state of lowest free energy of the capsules is decisively determined by the interplay between

hydrophobic and electrostatic forces and thus the total charge of the shell. Depending on this charge either surface tension, due to an unfavorable polymer/solvent interaction, or electrostatics dominate, leading to a shrinkage or expansion and subsequent rupture of capsules, respectively, at temperatures above the glass transition temperature ( $T_g$ ). For swelling capsules the force balance can be shifted by the addition of salt and subsequent screening of charges, which enables a reversible switching between shrunk and swollen states. The shrinkage of capsules is accompanied by a wall thickness increase. At the end-point capsules form dense smooth spheres. A new method to quantitatively analyze transmission X-ray micrographs of capsules recorded in aqueous environment indicates that the multilayer walls loose about 40% of their water content during capsule shrinkage.

As the permeability of the shells is distinctly decreased after heating due to the wall thickness increase and densification, a simple and universal encapsulation technique based on the heat treatment of capsules was developed. This new method allows the entrapment of differently charged molecules within a broad range of molecular weights into various kinds of capsules. The encapsulated amount has been quantified. It could be shown that polyelectrolyte multilayer capsules can fuse at temperatures far above  $T_g$  or at ionic strength far above the glass transition ionic strength without leakage of their content. From the microscopic snapshots a proper model based on different forces acting on the shells and temperature and salt induced fusion are proposed.

Due to potential applications in the fields of sensors or actuators, stimuable microcontainers and controlled drug delivery. Polyelectrolyte microcapsules containing stimuli-responsive polymers have been prepared with the focus on pH-sensitivity and carbohydratesensing.

First, pH-responsive polyelectrolyte capsules were composed of poly(allylamine hydrochloride) (PAH) and poly(methacrylic acid) (PMA) or poly(4-vinylpyridine) (P4VP) and PMA and varied considerably in their hydrophobicity and the influence of secondary interactions. These polymers were assembled onto  $\text{CaCO}_3$  and  $\text{SiO}_2$  particles with diameters of 5  $\mu\text{m}$ . Capsules were stable over a wide pH-range and exhibited a pronounced swelling at the edges of stability, which was attributed to uncompensated positive or negative charges within the multilayers. The swollen state could be stabilized when the electrostatic repulsion was counteracted by hydrogen-bonding, hydrophobic interactions or polymeric entanglement. This stabilization made it possible to reversibly swell and shrink the capsules by tuning the pH of the solution (**Fig. 2**) [2]. The pH-dependent ionization degree of PMA was used to modulate the binding of calcium ions. In addition to the pH-sensitivity, the stability and the swelling degree of these capsules at a given pH could be modified, when the ionic strength of the medium was altered. A theoretical model was proposed to explain the pH-dependent size variations that took into account an osmotic expanding force and an elastic restoring force to evaluate the pH-dependent size changes of weak polyelectrolyte capsules.



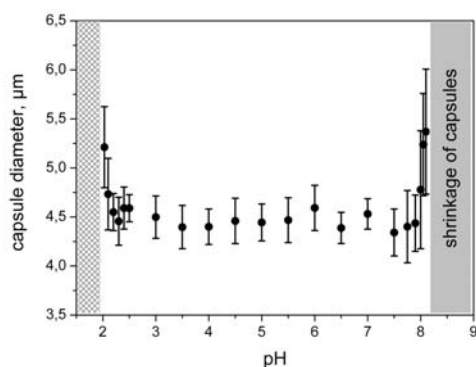


Fig. 2: Diameter of (P4VP/PMA)5 capsules as a function of pH (a). The shaded area indicates the region in which the capsules dissolved ( $pH < 2$ ). At  $pH > 8.1$  the capsules shrunk to particle-like structures.

Second, sugar-sensitive multilayers were assembled using the reversible covalent ester formation between the polysaccharide mannan and phenylboronic acid moieties that were grafted onto poly(acrylic acid). The resulting multilayer films were sensitive to several carbohydrates, showing the highest sensitivity to fructose. The response to carbohydrates resulted from the competitive binding of small molecular weight sugars and mannan to the boronic acid groups within the film, and was observed as a fast dissolution of the multilayers when they were brought into contact with the sugar-containing solution above a critical concentration. It was also possible to prepare carbohydrate-sensitive multilayer capsules, and their sugar-dependent stability was investigated by following the release of encapsulated rhodamine-labeled bovine serum albumin.

To drastically decrease the permeability of polyelectrolyte multilayered capsules and, therefore to make them enough efficient for encapsulation of small molecular species a perspective approach is based on use of dense polymers (polypyrrole) [3]. The polyelectrolyte shell modified by polypyrrole provides the capsule shell with water-resistant and sufficient barrier properties. However, relevant high brittleness of polypyrrole coatings demands more gentle capsule processing conditions. Magnetite iron oxide nanoparticles were used as a shell constituent to provide the capsules with magnetic properties and, therefore, to propose a mild technical protocol for capsule treatment.

Polyelectrolyte capsules containing metal (Ag- or Au-) nanoparticles in the shell are addressable optically. Focusing a laser on the capsule leads to capsule wall rupture. The potential of this method has been demonstrated on laser-induced release of encapsulated material from polyelectrolyte multilayer capsules inside living cells. Metal nanoparticles were incorporated inside the walls of the capsules, and served as energy-absorbing centers for illumination by laser light. Fluorescently labeled dextran was successfully incorporated into the capsules using the heat-shrinking method. The capsules obtained by such a method exhibit improved mechanical stability being important for the delivery of encapsulated material. Upon illumination by laser light, the encapsulated dextran leaves the interior of a capsule inside a living

cancer cell. Capsules not internalized by the cells are pushed up by the laser and move away from the field of view upon laser illumination from the bottom (Fig. 3) [4]. This study serves as a significant step toward the use of polyelectrolyte multilayer capsules for the delivery of medicine into biological cells, and is, therefore, relevant to research on drug delivery.

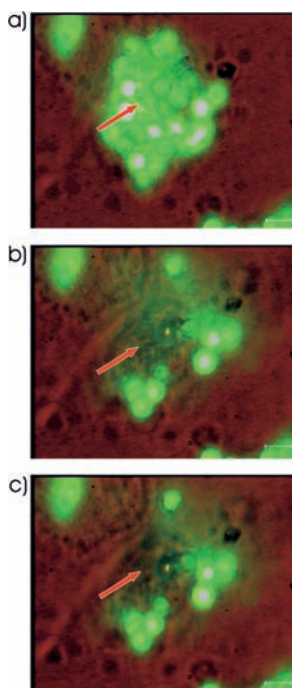


Fig. 3: Fluorescence images demonstrating the lifting up of noninternalized capsules located on top of a living MDA-MB-435S cell above and away from the imaging plane or the focus a) before, b) during, and c) after the laser beam illuminated the chamber from the bottom. The capsules were lifted up with a laser power of 50 mW. The red arrows indicate the locations of the capsules that were lifted up. The scale bars in all images correspond to 5 μm.

To mimic natural processes porphyrin nanotubes have been grown on microcapsules with well-defined thickness and length [5]. The tubes protrude from the capsule surface in an organized radial manner. These results suggest that an organized system of nanotubes and capsules can be obtained by using a simple method. Such porphyrin nanotubes can act as optical waveguides to propagate luminescence from one end of the tube to the capsule wall or interior; meanwhile, the capsule wall/interior can be suitably modified to utilize this energy. Hence, such a nanotube/microcapsule system should be able to mimic the architecture of chlorosomes, which are light-harvesting complexes in green photosynthetic bacteria.

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## Ordering of Functionalized Nanoparticles



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The self-assembly of colloidal particles allows for the construction of highly ordered structures on all length scales and for modeling the interactions between particles. Self-assembly is the hallmark of supramolecular chemistry, in which molecular components are spontaneously organized via covalent or non-covalent interactions into hierarchical structures having the complexity of the structures observed in nature. Compared with dazzlingly diverse supramolecules, the self-assembly of colloidal particles is rather simple. This simplicity arises primarily from the fact that the surface chemistry of colloidal particles is isotropic, leading to isotropic interaction between the particles. There is therefore little control over the spatial association between the particles. To circumvent this challenge, colloidal particles need to be imparted with the same moments of anisotropic interaction, or “valences” as atoms and molecules. In this way colloidal particles can be directed to organize by design [1]. Accordingly, the objective of our research activities is to fabricate new functional particles or to patch particles with new surface functionalities so as to fabricate colloidal “atoms” or “molecules”. We therefore aim to translate the language of molecular and supramolecular chemistry to govern the integration of colloidal particles in a spatially and temporally controlled manner.

## A. Interfacial Self Assembly of Nanoparticles

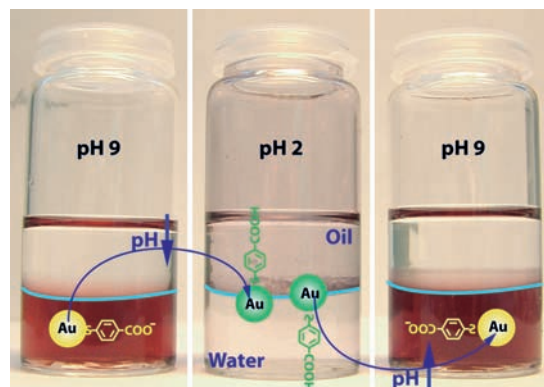


Fig. 1: pH-responsive interfacial self-assembly of aqueous 6 nm gold nanoparticles, stabilized by mercaptobenzoic acid. In the glass vial, the bottom phase is water and the top phase is heptane.

The unique characteristic of self-assembly encountered in nature is that it is dynamic, (i.e. assembly and disassembly occurs in a controlled manner). Contrastingly, the self-assembly of colloidal crystals is static and once the particles are associated, they can not be induced to dissociate. Using the water-oil interface as a platform for the self-assembly of charged hydrophilic nanoparticles, we have demonstrated that these assemblies exhibit characteristics of dynamic self-assembly [2]. Decreasing the surface charge density of charged nanoparticles results in an increase of their surface hydrophobicity, leading to the spontaneous assembly of those particles at the interface. If the particles were smaller than 15 nm, electrostatic repulsion between the particles, due to an increase in their surface charge density, was sufficient to redisperse the particles and pull them back to the bulk water phase (Fig.1). The reversibility of the interfacial assembly of nanoparticles may be due to the fact that the interfacial attachment energy of particles of a size less than 15nm is comparable to the thermal energy of those particles, resulting in a high sensitivity to energy variations of the system. The switchable surface wettability of the nanoparticles is central to their success as dynamically self-assembling materials.

The interface between water and oil provides a unique two-sided platform that enables a combination of chemistry in the aqueous and organic phases to be employed. Specific interactions, such as inclusion between a cyclodextrin and adamantine, and DNA-base pairing were used to direct nanoparticles to self-assemble at water/oil interfaces. Subsequently the surface chemistry of the particles was altered to deposit different nanoparticles onto the interface and form a heterogeneous structure with respect to both sides of the interface [3].

## B. Facet-Selective Growth and Organization of Nanoparticles

Additionally, different facets of nanoparticles may be used to direct the spatial association of those particles. To achieve the facet-selective self-assembly of colloidal particles, the

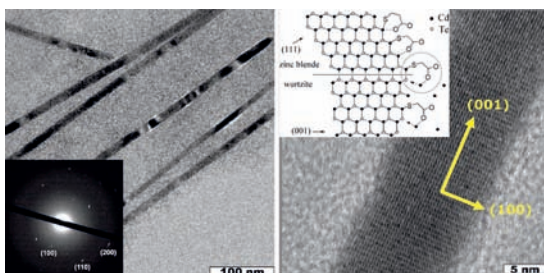


Fig. 2: Aqueous wurtzite CdTe nanorods derived from secondary coordination of thioglycolic acid.

different facets should be well defined and spatially segregated on the particles. In this context, non-spherical shapes are ideal. Recently, we systematically explored the influence of various experimental variables such as temperature, stabilizer chemistry, precursor concentration, and pH on the growth of semiconductor nanocrystals in aqueous media [4]. Due to the interaction between different ligands, colloiddally stable one dimensional (1D) CdTe nanostructures such as nanorods and nanowires were successfully fabricated, providing building blocks for facet-selective self-assembly (Fig.2).

## C. Stereo-Decoration of Au Nanodots on Micro-Spheres

To transform colloidal particles into colloidal “atoms” or “molecules”, a straightforward but challenging way is to pattern the particle surfaces. However, conventional lithographic techniques only pattern planar surfaces due to the lack of appropriate masks for highly curved surfaces. We recently succeeded in developing a colloidal lithographic method that uses the interstitial gaps in the upper layers of colloidal crystals as masks for depositing Au vapor onto spheres in the lower layers [5]. Using anisotropic reactive ion etching and azimuthally offset vapor deposition, well-controlled numbers of Au nanodots were selectively deposited on different regions of the microspheres (Fig.3). The number of Au dots was determined by the structure of the colloidal crystal template, the size of the template spheres and experimental variables such as the etching time and the incident angle of the Au vapor. The spatial arrangement of the Au dots on the microspheres resembled the configuration of hybridized orbitals of carbon or silicon atoms. In this scenario, Au dots can be employed as “valences” to direct the spatial association of microspheres. This could pave a new way – colloidal valence chemistry – to organize colloidal particles into hierarchical structures with the complexity inherent in molecules or supramolecules.

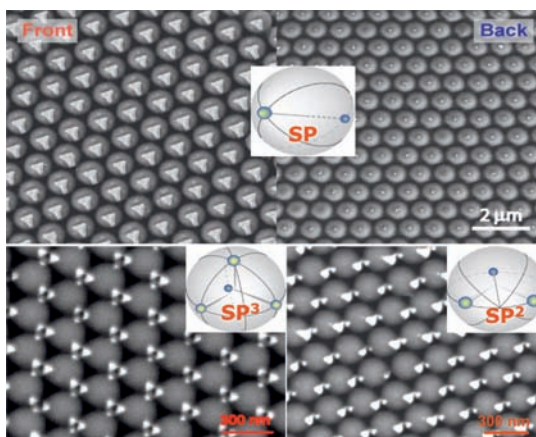


Fig. 3: Polystyrene microspheres decorated with 2, 3, and 4 Au nanodots, having spatial arrangements that are reminiscent of the hybridized orbitals of carbon atoms.

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# Molecular Assemblies of Biomimetic Systems and Nanostructures



## Aims

- Molecular assemblies of biomimetic systems: Membrane hydrolysis; Complex assembly of lipids, proteins, enzymes and biomolecular motors:  $F_0F_1$ , Kinesin, Actin; Biogenic microcapsules; Self assembly and in vitro characterization of biological molecules such as DNA, peptide and single cells as well as their mixtures with surfactant and polymers.
- Bio-interfaces: molecular patterns, surface modification, molecular recognition of enzymes, chemical recognition at cell surfaces, transport through cell membranes.
- Design and synthesis of bioinspired molecules and materials for drug release and gene delivery.
- Nanostructures: Design, synthesis, characterization and functionalization of nanoparticles, nanopatterns, nanotubes, nanocrystals.

## Results

### A. Molecular Assembly of Biomimetic Systems

#### • ATPase Assembled into Microcapsules for ATP Biosynthesis

The biomolecular motor, ATPase assembled in lipid-modified polyelectrolyte microcapsules enables to use the process of ATP biosynthesis as a novel routine to fabricate bionanodevices. This assembled complex can not only help us to understand the biological function of ATPase molecules but also provides a well-defined container for the storage of energy currency as an artificially designed system containing ATPase. When vital activities need energy, ATP will be released across the wall of the capsules as power supply (Fig. 1).

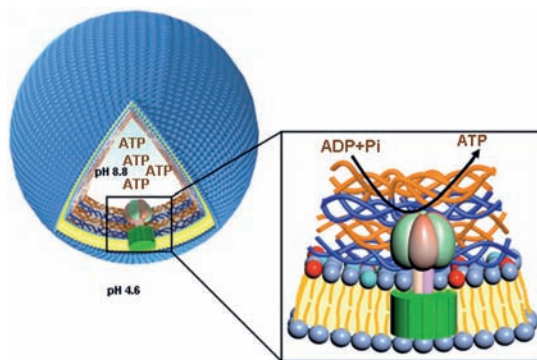


Fig. 1: Schematic representation of the arrangement of CFoF1-ATPase in lipid-coated microcapsules

#### • Assembled Peptide Vesicles for Gene Delivery and Release in Cells

The synthesized multivalent cationic peptide-lipid (MCPL) is considered for DNA delivery to mammalian cells. The MCPL can form dispersed liposomes. The binding of MCPL liposomes with DNA can be detected by a standard ethidium bromide (EtBr)-DNA fluorescence quenching assay. As such assembled DNA/EtBr/MCPL solution is incubated with trypsin. The fluorescence intensity increases after trypsin hydrolyzed the head-group of MCPL suggests the DNA release from the complexes. The high enhanced transfecting efficiency of MCPL with DNA is expected. We intend to design and synthesize several different types of cationic peptides for this purpose (Fig. 2).

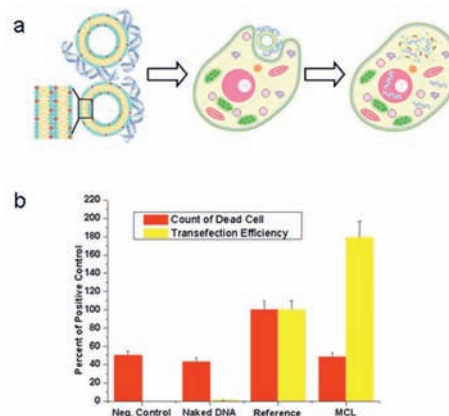


Fig. 2: (a) Schematic illustration of DNA release from cationic lipopeptide vesicles; (b) Gene transfection efficiency and cytotoxicity results after 48 h in HeLa cells

#### • Conversion of Dipeptide for Gene Delivery through the Cell Membrane

Positively charged dipeptides can self-assemble spontaneously into the structure of vesicles under a certain condition. Such a conversion could readily bring genes into cells through the membrane. The self-assembly behavior of dipeptide nanostructure can be exploited as a new class of molecular transporter for the delivery of a wide range of foreign substances such as drugs and proteins. We are interested in investigating the conversion process quantitatively and building up models. Several relevant systems will be developed (Fig. 3).

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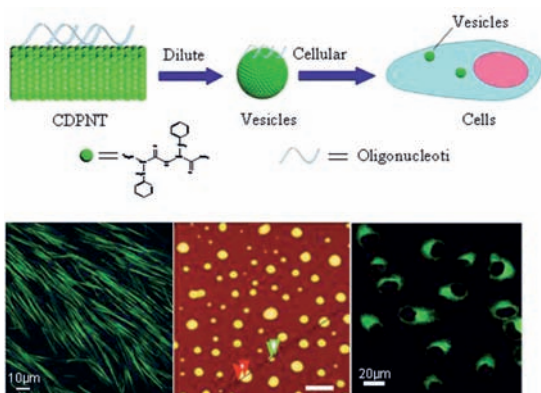


Fig. 3: Proposed mechanism of transition of the CDPNTs into vesicles for oligonucleotide delivery and corresponding microscopic results.

## B. Nanostructures

### • Protein Supported Lipid Patterns for the Targeted Recognition

Supported lipid micro-, nanopatterns are one of the most popular biomembrane models which can be applied to fundamental studies of cell membrane science and the engineering of integrated lipid membrane microdevices. Our aim is to fabricate stable lipid bilayer patterns to create the possibility of cooperating specific components like channels or receptors for specific recognition, which allows transferring materials (like drugs) to a solid surface for the medical application.

### • Template Synthesized Polymer Nanotubes

Most synthesized nanotubes exhibit a good perspective for application in the biological or medical field, for instance for bioseparations or materials transport. At this stage, precisely controlling the inner diameter and biocompatibility of the synthesized nanotubes is highly required. Template synthesized polymer nanotubes have the obvious features of high flexibility and mechanical stability. With the combination of self-assembly and layer-by-layer assembly techniques one can modify the inner pores in different way through electrostatic absorption, covalent bond, hydrogen bond or chemical reaction to obtain micro-nanosize tubes. The achieved nanotubes may contain the features of biocompatibility, luminescence, biodegradability or thermosensitivity, which promises the potential applications in polar cells, drug delivery, biocatalysis or tissue engineering (Fig. 4).

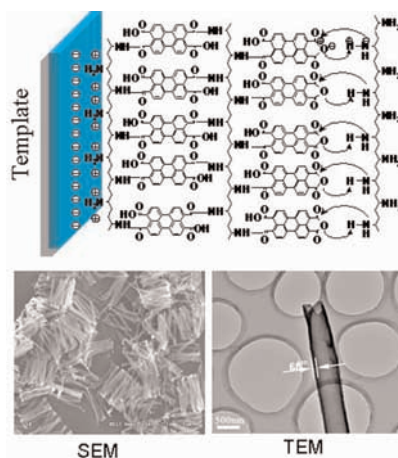


Fig. 4: SEM and TEM images of assembled multi-functional composite nanotubes via covalent bond

### • Decoration of Gold Nanoparticles

The nanocomposites of gold nanoparticle (AuNPs) with various macromolecules display much potential applications in the fields of biology and nanotechnology. Surface-initiated atom-transfer radical polymerization on the AuNP surface provides a perfect core-shell nanostructure and will alter the property of nanoparticles and response to interface and environment. Such nanosized hybrids are considered for delivery of biomolecules, catalysts or drugs (Fig. 5).

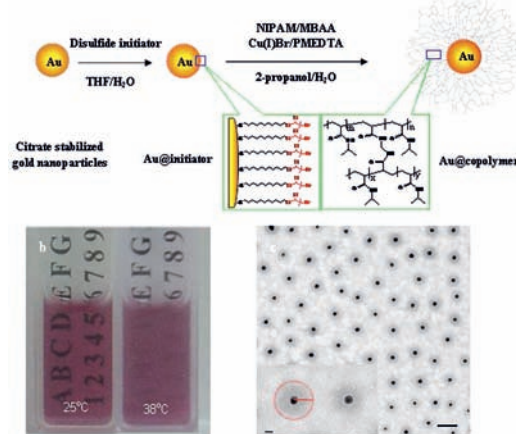


Fig. 5 (a) Scheme of the preparation of Au@PNIPAM nanoparticles by the ATRP procedure; (b) Optical photos of Au@copolymer hybrids with 1% MBAA at 25 and 38°C, respectively; (c) TEM image of Au@copolymer hybrids with 1% MBAA to encapsulate 3.5 nm gold nanoparticles. Scale bar = 20 nm.

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### Hybrid MPG/FhG Research Group “Nanotechnology for Life Science” & Golm Campus Initiative “Bioactive Surfaces”



Within the last few years, the Max-Planck society and the Fraunhofer society have established a successful collaboration program in the science park of Golm. Such joint collaboration MPG/FhG is almost unique in Germany and combines the complementary skills of both institutions (i.e. fundamental and applied research) for developing novel generations of applied materials.

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Thesis: Anionic polymerization of phenyl glycidyl ether in miniemulsion

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The first initiative was the creation in April 2002 of the group “Nanotechnology for Life Science”, a hybrid research team between the Fraunhofer Institute for Applied Polymer Research (IAP) and the Max Planck Institute of Colloids and Interfaces. The team is currently lead by Dr. Jean-François Lutz and combines fundamental research and applied projects with industrial partners (e.g. Schering A.G., Qiagen GmbH, Capsulation). For instance, the team focuses principally on potential applications of macromolecules in all aspects of human medicine (delivery, diagnostics, biomaterials). A first objective is to prepare at the molecular level novel macromolecules with a life science potential, such as water soluble polymers, amphiphilic copolymers, biodegradable polymers, polymer bioconjugates or stimuli responsive polymers. For reaching this goal, several modern methods of synthesis such as controlled radical polymerization, living polymerization of polypeptides, ring opening polymerization or click chemistry are combined [1-4]. All these methods constitute an original “macromolecular toolbox”, which permit to synthesize macromolecules with a tailor-made molecular structure (i.e. controlled chain-length, molecular weight distribution, composition, architecture and functionality) and unprecedented properties. A good example of such synthetic work is the recent design of thermoresponsive polymers based on biocompatible oligo(ethylene glycol) segments [5,6]. The stimuli-responsive behavior of these new polymers can be precisely controlled by simply varying their molecular structure. Moreover, in comparison to standard thermoresponsive polymers (e.g. PNIPAM) these novel structures possess the advantage to exhibit a reversible phase transition. Such “smart” and biocompatible macromolecules possess a very high potential for bio-applications.

Besides applied polymer chemistry, the group “Nanotechnology for Life Science” focuses intensively on nanomaterials design. The team develop tailor-made 2D (functional surfaces) or 3D (nanoparticles) nanostructures for a large range of medical applications such as bioseparation, controlled drug delivery, non-viral gene delivery or magnetic resonance imaging. Various types of colloidal nanostructures were prepared and studied during the last few years such as nano-aggregates capable to transport DNA into living cells (polyplexes), microgels utilizable for controlled drug delivery, stealth-nanoparticles, which can be used in several aspects of nanobiotechnology, and micellar assemblies (micelles, vesicles), which possess an enormous applicative potential as nanocontainers for drug delivery [7-10].

The success of the “Nanotechnology for Life Science” initiative confirmed the complementary roles of Fraunhofer, Max-Planck Institutes and University Potsdam within the Research Campus Golm. Thus in 2007, this dual collaboration will be transformed into a bigger campus network “Bioactive Surfaces” sponsored by both Fraunhofer and Max Planck Societies. The goal of this new project is to create a strong local research force for developing novel generations of bioactive surfaces (i.e. colloidal or flat model surfaces) capable of interacting “on demand” with biological systems such as DNA, proteins, enzymes or cells. **Fig. 1** summarizes the scientific strategy of this research program. The main scientific objectives are both fundamental and applied. This project is designed for studying the fundamental aspects of bioactive surfaces and moreover for transforming this basic knowledge into marketable applications. In that regard, the proposed cooperation between Max Planck Institutes and Fraunhofer Institutes is ideal.

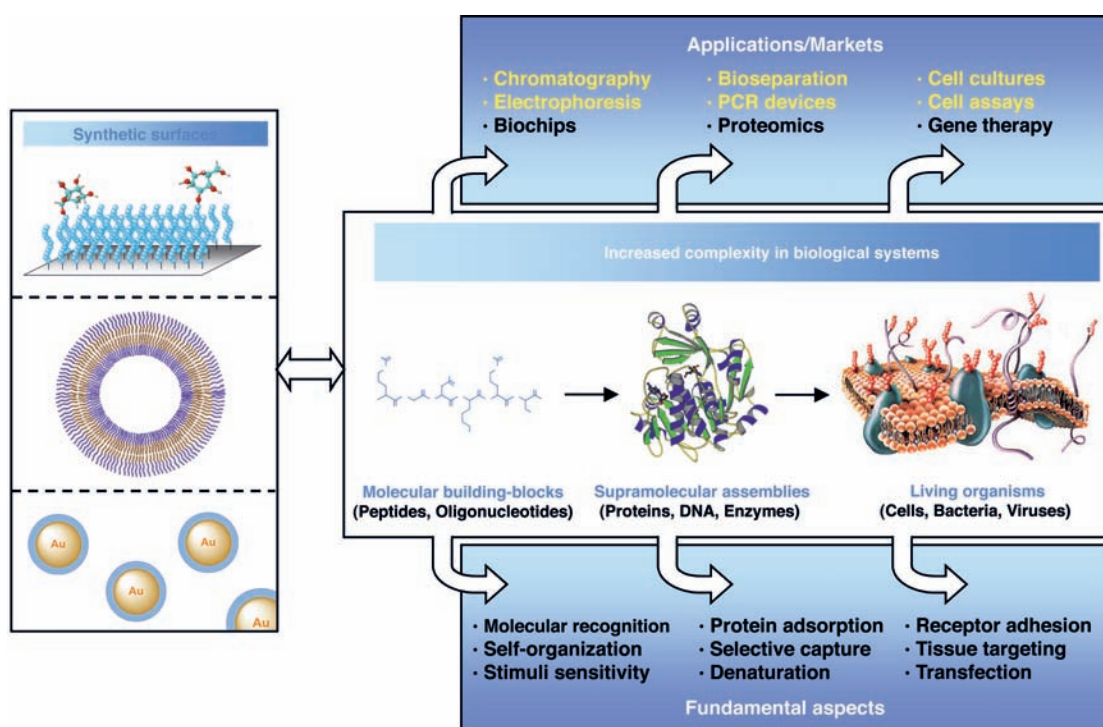


Fig. 1: Schematic description of the main fundamental and applied issues of the campus project "Bioactive Surfaces". The left part of the graphic represents examples of flat or colloidal synthetic model surfaces. The right part of the graphic lists the biological systems, which will be investigated in this program. The applications highlighted in yellow will be principally studied within the time frame of the campus project.

Three main scientific aspects will be explored in this project: (a) The development of specific interactions between synthetic surfaces and biological systems. (b) The control of conformational variations using artificial surfaces. (c) The preparation of stimuli-sensitive surfaces capable of interacting "on demand" with biological systems. For solving such complex scientific issues, a multidisciplinary network is indeed necessary. Thus, this project combines all the complementary competences present in the Science-Park Golm: theory, polymer chemistry, biochemistry, colloidal physico-chemistry, physics of interfaces, biology and applied biotechnology. More precisely, this novel interdisciplinary network will involve active collaborations between the Fraunhofer Institute for Applied Polymer Research (Research group Nanotechnology for Life Science), the Fraunhofer Institute for Biomedical Engineering (IBMT), the Max Planck Institute of Colloids and Interfaces (theory, colloids and interfaces departments) and the Institute of Physical Biochemistry of the University of Potsdam.

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