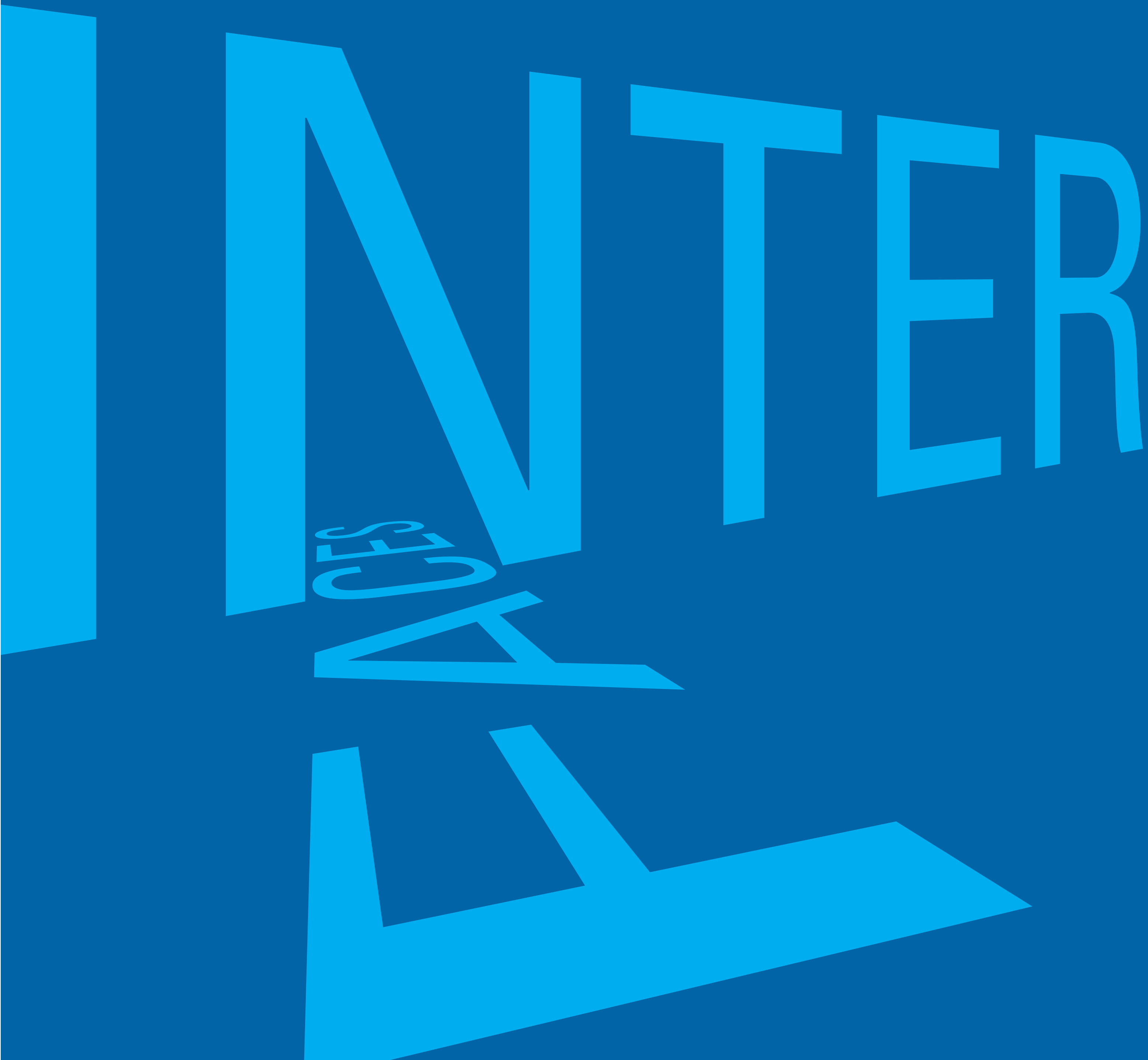
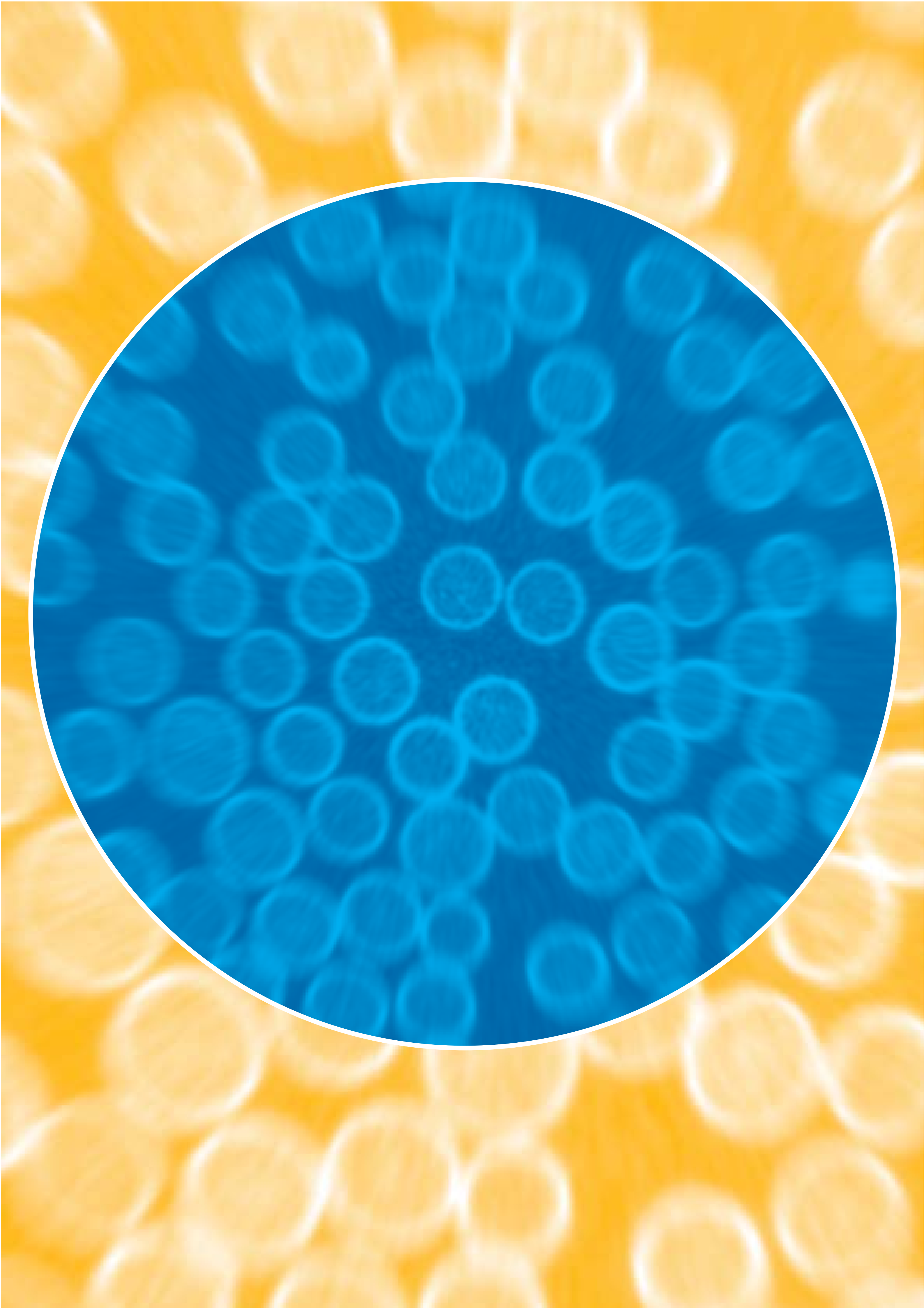
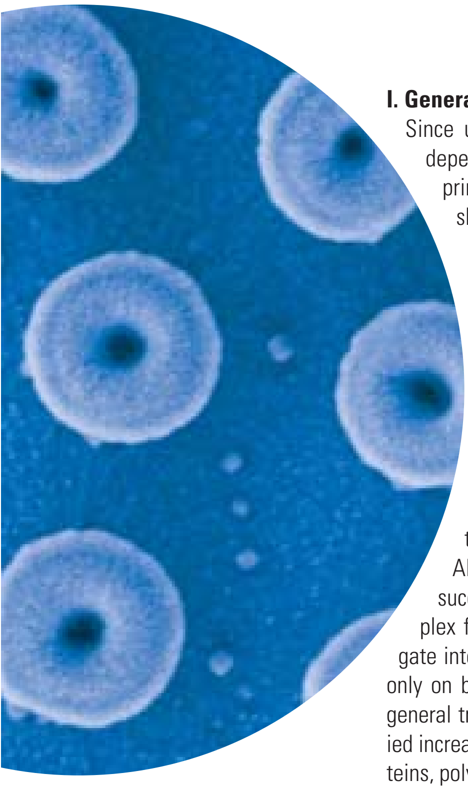
INTERFACES





Research in the Department of Interfaces



I. General Strategy

Since understanding colloidal systems to a large extent depends on understanding their internal interfaces the prime motivation of the department of interfaces is to shed light into structure, forces and dynamics of molecular interfaces. Traditionally this has been achieved by developing more and more refined methods to analyze planar air/water and oil/water interfaces, and these developments are still continued. Some of these like optical, dynamic surface tension and scanning probe microscopy measurements have also been appreciated much by colleagues that they became commercialised by start-ups. It is in the spirit of the institute that much of the knowledge gained with planar interfaces can be transferred towards interfaces in colloidal systems. Along this line the department has started with great success to study also coated colloids, capsules and complex films which in turn opened new avenues to investigate interfaces by techniques which are typically applicable only on bulk systems (NMR, DSC, flash spectroscopy). As a general trend the reader may realize that the interfaces studied increase in complexity, i.e. they also contain peptides, proteins, polymers and nanoparticles, and only in rare cases interfaces with only low molecular weight detergents are studied.

Research within the department is organized within groups of size between 2 and 10 people that are led by a staff scientist. They are rather independent from the director as regards specific research topics and means. In addition I supervise directly some students and postdocs to venture new areas and try to stimulate making use of synergies within the department, the institute or with outside groups by allocating proper internal funds and advising in getting external funding.

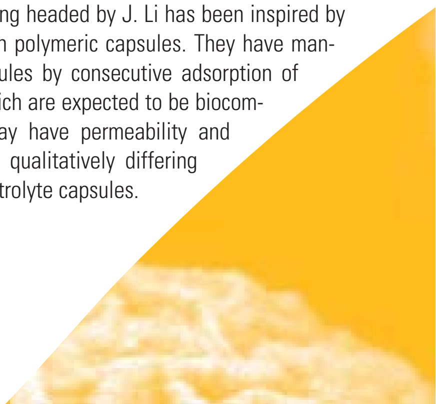
II. Research Highlights

II.1 Planar Interfaces

About half of the activities of the department concern amphiphiles at planar liquid interfaces. Among them insoluble monolayers still maintain a dominant role because of their high definition as model surfaces. Since phase diagrammes are meanwhile understood reasonably well they can now be used to study the interaction with components in the third dimension for which most modern techniques have been developed (FTIR-spectroscopy, X-ray diffraction, X-ray, Neutron reflectivity). Highlights of the Brezesinski group concern (i) the Mg^{2+} mediated DNA binding to zwitterionic phospholipid monolayers enabling a nematic DNA alignment (ii) the modulation of phospholipase activity via reaction products changing the monolayer structure and (iii) the influence of hydrophobic surfaces on peptide conformation (including β-amyloid). The insoluble monolayer is also most suitable to study ion distribution near charged surfaces, and along this line the Motschmann group has been successful demonstrating by ellipsometry an ion condensation transition with increasing amphiphilic surface density. This group in collaboration with that of D. Wantke has also developed a dynamic surface tension measurement system covering a frequency range from 1 to 1000 Hz. They have coupled this with measurements of second harmonic generation to discriminante between lateral compressibility and molecular exchange with the bulk phase. As the most basic and far-reaching result of the Motschmann group I consider sum frequency measurements of hydrogen bonds at interfaces. They indicate that breaking and reformation are dominant energy dissipation mechanismus which may in turn be related to the old unsolved problem of foam stability. The group of R. Miller has been concentrating on modelling of thermodynamics and dynamics of lipid/protein systems, and it appears that differences in the protein flexibility can be explained. The work on "Thin Liquid Films" has seen a transition from H.-J. Müller to R. v. Klitzing where polymers and particles between two interfaces gained importance, and where the most important results concerned oscillatory force/distance relations indicating a layering of these components. As regards crystallization and growth at interfaces the work of H. Riegler started with the most simple systems, alkanes on SiO_2. It has shown the distinction between two- and threedimensional growth processes and will develop towards nanostructured surfaces and more complex molecules.

II.2 Nonplanar Interfaces and Complex Films

From the work on nonplanar surfaces and complex films I consider most ground-breaking that of the group of D. Wang who could synthesise polymer brushes of different chemistry on a variety of nanoparticles (Au, Ag, Fe_2O_3) and who could thus design their wettability and solubility. The work of the Sukhorukov group on polyelectrolyte multilayer capsules has been successful in demonstrating ways to change the permeability, making stimuli sensitive capsules, crystallizing inorganic particles in the walls or inside. They also demonstrated biomineralization within confined space, i.e. growing minerals via an enzymatic reaction. Of some application potential is the remote controlled opening of capsules via focused light, ultrasound or microwaves. The Fery group has now in routine operation the combination between colloidal probe force measurements and reflection interference contrast microscopy. This enables understanding of capsule deformation by comparison of data with finite element analysis. They now discovered abrupt changes of elastic moduli with salt concentration and also developed a technique to measure film mechanics by preparing ultrathin freestanding polymer films covering hole areas of variable but defined diameter. The construction of mesoscale supramolecular systems in the Kurth group has led to unusual magnetic properties. They are related with the metal (Fe^{2+}) coordination shell in the supramolecular modules that is changed if the system undergoes a phase transition. D. Kurth has in addition become director of a joint lab in Tsukuba where the focus will concern synthetic chemistry. The international joint lab in Beijing headed by J. Li has been inspired by the great success with polymeric capsules. They have managed to prepare capsules by consecutive adsorption of proteins and lipids which are expected to be biocompatible and which may have permeability and mechanical properties qualitatively differing from those of polyelectrolyte capsules.



III.3 Cooperations

The department has developed in-house collaborations not only as regards sharing methods but also in order to gain knowledge, e. g. on interfacial crystallization, micro- and nanomechanics. The outside collaborations were motivated either by pursuing specific projects, getting access to specialized techniques or developing a system towards applications. The latter case is not the mission of the institute but we feel obliged to support others activities.

Close collaborations have been arranged with all universities in the Berlin/Potsdam area and with Neutron (HMI) and Synchrotron sources (BESSY, HASYLAB). In addition a joint laboratory on "Polymeric Nanotechnology for Life Sciences" has been established together with the neighbouring "Fraunhofer Institute for Applied Polymer Research". This should bring our work closer to applications, and the group had developed especially close links to the Charité (Prof. Pison). The department has also been most successful to acquire cooperative projects in competitive programmes of the VW foundation (Complex Systems) and of the BMBF (Bionanotechnology). The many partners there as well as those of our German/French collaborative research group are listed under fundings.

IV. Past and Future Development

I regret having lost many staff scientists in the last 2 years:

- G. Czichocki and H.-J. Müller retired
- T. Fischer accepted a call as professor of chemistry at Tallahassee, Florida State Univ.
- M. Schönhoff has become professor of applied physical chemistry at Univ. Münster
- R. v. Klitzing has become professor of physical chemistry at Univ. Kiel
- G. Sukhorukov accepted a call on a chair of biomaterials at Queen Mary University London.

These are of course losses on a personal level as well as of scientific skills and experience. On the other hand it provides flexibility to start new directions and to redirect existing ones. In addition it has enabled to reduce the department's size from more than 100 to about 75 people. With some delay the shrinking will continue by another 10 persons, and this is also urgently needed due to a lack of space.

Those four young scientists leaving on professor positions will move much of their activity with them. This is clearly in the interest of the institute, but the question remains what is left in the department?

The work on foam films by H.-J. Müller has partly entered in R. v. Klitzing's group. With her leaving studies on wetting liquid films and polyelectrolyte/lipid films will be continued under the guidance of R. Krustev. Well trained and highly motivated graduate students and postdocs of the Sukhorukov group will remain in the department for at least another 2 years. For the time being it remains open if there will be another group leader. In any case the physical aspects of film permeation and molecular recognition at surfaces will remain an important issue for the department. Driven by personnel experience I will also be engaged more directly in aspects of targeted drug delivery.

Another topic concerns making use of synergies by collaboration of existing groups on a new topic. One of this will be the study of nanoparticles at interfaces. For microparticles Pickering emulsions are known since 100 years, and they are rediscovered in the US literature as colloidosomes. Their excitement also results from the fact that well-defined particles can be prepared and observed directly. The development in D. Wang's group now yields well-defined nanoparticles which can be adsorbed at interfaces to yield "nanoparticlosomes" with presumably interesting mechanical and permeability properties where interparticle interactions and dynamics can be studied by those methods hitherto used for amphiphilic molecules. The department has a lead in the combination of most modern methods and I hope it will be able to make use of it selecting this new and exciting topic.

Helmuth Möhwald
Director of the Department of Interfaces

Interactions in Complex Monolayers

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Thesis: The parametric pump – a physical-chemical model of the active transport of ions in cells
1981: PhD, Physical Chemistry
(Martin Luther University of Halle/S.)
Thesis: Einfluss der chemischen Struktur auf das thermische Phasen- und Mischungsverhalten binärer und ternärer Phospholipid-Wasser-Systeme
1987: Habilitation, Colloid Chemistry
(Martin Luther University of Halle/S.)
Thesis: Untersuchungen zum Phasen- und Mischungsverhalten ausgewählter Phospholipid-Wasser-Systeme
1981-1982: Postdoc (Biological Research Centre, Szeged, Hungary)
1982-1992: Research Scientist
(Institute of Physical Chemistry, University of Halle/S.)
1992-1995: Research Scientist
(Institute of Physical Chemistry, University of Mainz)
Since 1995: Group Leader
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Nonviral DNA Transfection

[in cooperation with B. Dobner (Halle), E. Donath (Leipzig), E. Rogalska (Nancy)]

Aim: Direct gene transfer has become increasingly important for the development of therapies for human diseases. Nonviral gene transfection represents an alternative approach to viral vectors. However, this method is still not efficient enough. This work aims to improve our knowledge about the structure of DNA/lipid complexes.

Results: Cationic lipids form stable and structured complexes with DNA. However, such complexes are frequently toxic for the cell. Complexes composed of neutral (zwitterionic) lipids offer an alternative as they are completely non-toxic. Neutral lipids do not interact with DNA directly, but the interaction can be mediated by divalent cations. The presence of adsorbed DNA was verified by IRRAS (Infrared Reflection Absorption Spectroscopy) as well as GIXD (Grazing Incidence X-ray Diffraction) experiments. IRRAS shows the typical bands of DNA only in the presence of divalent cations. The presence of DNA *and* magnesium ions leads to a reduction of the tilt angle of the zwitterionic DMPE (1,2-dimyristoyl-phosphatidyl-ethanolamine). Additionally, the adsorption of DNA occurs in an ordered way and leads to the appearance of an additional Bragg peak. Compression from 10 to 40 mN/m decreases the d-spacing of the ordered DNA strands from d=4.6 nm to 4.3 nm. Assuming that the length of the DNA strands is not influenced by compression, the area per charge (0.17 nm/e$^-$ times d) of the DNA decreases only by around 6.5 % during the compression **(Fig. 1, left)**. The comparison of the area per charge of DMPE and DNA indicates that two DMPE molecules (1 elementary charge per lipid head group) are coupled to one elementary charge of the DNA **(Fig. 1, right)**.

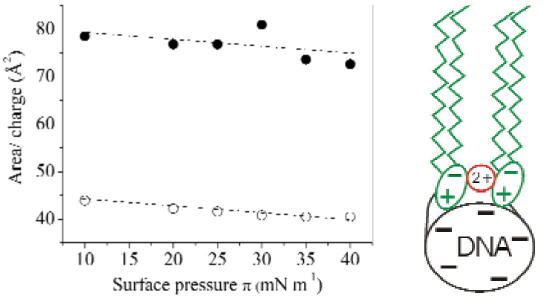

Fig. 1: (left) Area per elementary charge as function of surface pressure π of calf thymus DNA (●) and DMPE (○) as deduced from GIXD. (right) Schematic representation of DNA–DMPE interaction mediated by divalent cations

Additionally, the monolayer behavior of lipids with a new core structure and different basic head groups has been investigated. Depending on the pH values, the head groups can be in a fully protonated (charged) state. All amines form stable monolayers at the air/buffer (pH 4) interface. GIXD experiments show that the tilt of the aliphatic chains depends strongly on the head group structure. The tightest packing (rectangular, non-tilted chains, cross-section of the chains = 19.5 Å^2) was observed for N-(2-aminoethyl)-N´-2-dihexadecylpropane-diamide.

An additional Bragg peak can be seen at 1.326 Å^{-1} corresponding to d = 4.74 Å indicating the formation of hydrogen bonds **(Fig. 2)**. All investigated amide lipids bind DNA. Adsorption of DNA leads to a fluidization of the monolayer. A one-dimensional periodicity between coupled DNA strands has been observed. The distance between the ordered DNA strands is independent on pressure and head group structure (3 nm < d_{DNA} < 3.3 nm).

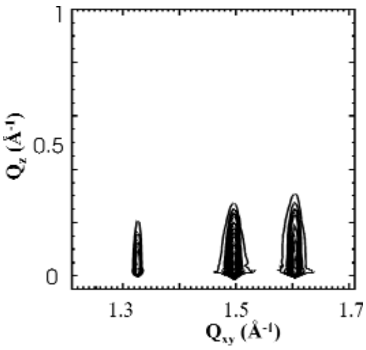

Fig. 2: Contour plots of the corrected X-ray intensities as function of the in-plane (Qxy) and the out-of-plane (Qz) scattering vector components of N-(2-aminoethyl)-N´-2-dihexadecylpropanediamide taken at 20 mN/m and 20 °C.

Adsorption of Amyloid Beta (1-40) Peptide on Different Surfaces

[in cooperation with A. Thünemann (Berlin), R. Krastev (Potsdam), A. Blume (Halle)]

Aim: Amyloid beta (1-40) peptide folding into beta-sheet containing fibrils is thought to play a causative role in Alzheimer's disease. The adsorption at surfaces was always associated with a transition of the secondary structure of the peptide. Therefore, the amyloid fibril formation may be driven by interactions with surfaces.

Results: Due to its amphiphilic character Amyloid beta (1-40) peptide adsorbs to the air/water interface and penetrates into weakly compressed lipid monolayers. Langmuir monolayers of negatively charged as well as of zwitterionic phospholipids have been used to study the influence of the peptide on the lipid packing and vice versa the influence of the lipid on the peptide secondary structure by means of IRRAS and GIXD. Being adsorbed at the interface, the peptide adopts beta-sheet conformation oriented parallel to the surface **(Fig. 3)**.

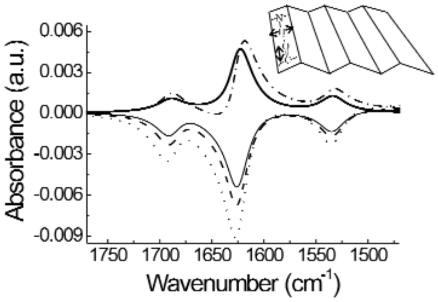

Fig. 3: Simulation of IRRA spectra (p-polarized light, angle of incidence between 32° and 62°, Amide I bands at 1627 and 1690 cm^{-1} and the Amide II band at 1535 cm^{-1}) of a beta-sheet secondary structure lying flat at the air/water interface. The measured spectra agree very well with the simulated ones.

Compression of the lipid monolayers with inserted peptide leads to the squeezing out of the peptide at higher surface pressures (> 30 mN/m). The peptide desorbs completely from zwitterionic and negatively charged monolayers on buffer, although it remains adsorbed in beta-sheet conformation at negatively charged monolayers on water. This can be explained by electrostatic interactions with the lipid head groups. Additionally, the peptide does not influence the lipid structure at physio-logical pH and modest ionic strength.

The adsorption of Amyloid β-peptide at solid/liquid interfaces was characterized by neutron reflectometry. Distinct polymeric films were used in order to obtain different surfaces: charged and non-charged hydrophilic surfaces as well as hydrophobic layers. Amyloid β-peptide was found to adsorb on positively charged and hydrophobic surfaces as deduced from the shift of the minima in **Fig. 4**, whereas no adsorbed layer was detected on hydrophilic non-charged and negatively charged films. The peptide adsorbed on the positively charged film as patches dispersed over the surface, whereas a uniform and tightly packed layer, which did not contain water, was observed on hydrophobic surfaces.

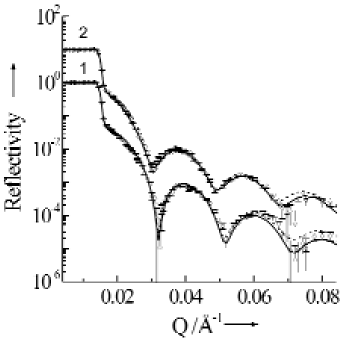

Fig. 4: Neutron reflectivity of a charged PEI/(PSS/PAH)$_6$ film in D_2O: 1) bare polymer surface; 2) polymer surface exposed to Amyloid beta (1-40) peptide solution for 12 h. The curves are offset for clarity.

Enzymatic Reactions at Interfaces

Aim: Phospholipases (PL) are widespread enzymes that hydrolyze phospholipids. The application of sophisticated monolayer techniques such as GIXD and IRRAS has contributed much to our knowledge about the interaction of PL with phospholipid monolayers. However, it has remained obscure which lipid parameters, including head group conformation, lipid chain order and tilt, are crucial for PL activity.

Results: Phospholipase D (PLD) catalyzes the hydrolysis of phospholipids to phosphatidic acids. Previous experiments showed that PLD has maximum activity if the monolayer is in the liquid-expanded state. A model of product inhibition via modification of the substrate monolayer structure was deduced. This model was supported by the observation of a critical tilt angle of the substrate chains below which no hydrolysis was observed. Three different lipid systems (pure DPPC, DPPC/*n*-hexadecanol (1/1 mol/mol), and DPPC/1,2-dipalmitoylglycerol (1/1 mol/mol)) were used to determine the critical angle. At all surface pressures investigated, the chains of DPPC are tilted because of the large head group. In contrast, a non-tilted hexagonal lipid chain packing was observed for the mixtures. The double-chain lipid DPG is more efficient in forcing the DPPC molecules into the non-tilted conformation (25 mN/m instead of 45 mN/m for hexadecanol). The hydrolysis of DPPC catalyzed by PLD was investigated by IRRAS. There is no single critical tilt angle but a system specific one. Further experiments are necessary to verify this result.

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Key Publications:

[1] Symietz, C., Schneider, M., Brezesinski, G. and Möhwald, H.: DNA-alignment at cationic lipid monolayers at the air/water interface. Macromolecules **37**, 3865-3873 (2004).

[2] Gromelski, S. and Brezesinski, G.: Adsorption of DNA to zwitterionic DMPE monolayers mediated by magnesium ions. PCCP **6**, 5551-5556 (2004).

[3] Maltseva, E. and Brezesinski, G.: Adsorption of Amyloid beta (1-40) peptide to phosphatidylethanolamine monolayers. ChemPhysChem **5**, 1185-1190 (2004).

Thin Liquid Films

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Thesis: Studies on the Psychoacoustic Overshoot Effect
1996: PhD, Physical Chemistry
(Mainz University)
Thesis: Adsorption of Polyelectrolytes at Charged Interfaces, Molecular Transport and Ion Distribution within Polyelectrolyte Multilayers
1996-97: Postdoc,
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1998-2003: Assistant Professor,
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2003: Habilitation,
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Thesis: Structuring of Polyelectrolytes in Thin Films and Near Interfaces
2004: Group Leader,
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Since 2004: C3-Professor, Physical Chemistry (Kiel University)

Aims

Our research deals with the investigation of colloidal dispersions confined in thin liquid films (5 nm < h< 200 nm). The aqueous dispersions are either Silica suspensions or solutions containing polyelectrolytes of different molecular architecture (e.g. linear and branched). The investigated nanofilms are either symmetric (foam films and films between solid interfaces) or asymmetric (wetting films). In the focus of interest is the effect of geometrical confinement on the *inter*molecular (or interparticle) and *intra*molecular forces. Another important aspect is the effect of surface composition on the interactions within the *liquid* films. For this purpose liquid surfaces are modified by using different surfactant/polymer combinations and *solid* interfaces are varied by the deposition of polyelectrolyte mono- and multilayers.

Results

Intermolecular Interactions

The intermolecular interactions within the thin liquid films are studied by force measurements. In the case of foam films and wetting films the disjoining pressure is measured in a *thin film pressure balance (TFPB)* and the forces in a film between solid interfaces are studied in a *Colloidal Probe AFM*.

Above a certain concentration of the colloidal dispersion an oscillatory force curve is measured **(Fig. 1)**.

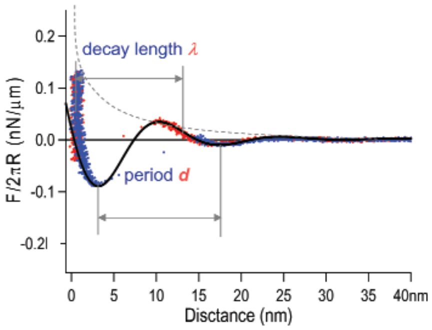

Fig. 1: Exemplary image of an oscillatoric force curve of an aqueous polyelectrolyte film confined in a Colloidal-Probe AFM.

In the case of spherical particles (Si particles or hyperbranched polyelectrolytes) the oscillation is explained by layer-by-layer expulsion of the particles. While for the "soft" polyelectrolyte particles the oscillation period is similar to the particle distance in the bulk ($\sim c^{-1/3}$), it is independent of the particle concentration in the case of "hard" Si particles. It is assumed that the deformability is responsible for this principle difference. In general, the conservation of the correlation length (distance between polyelectrolyte spheres, mesh size of a network of linear polyelectrolytes ($\sim c^{-1/2}$)) during confinement seems to be characteristic for "soft" additives, and the pressure period is dominated by electrostatic interactions **[1]**. "Hard" additives can be pushed together, and the pressure period is rather governed by the geometry of the particles. In current experiments, the limits of the theoretically predicted Manning condensation are checked for linear polyelectrolytes.

Intramolecular Interactions

Although the distance between linear polyelectrolyte chains remains constant during confinement, the chain conformation could be changed. This question is investigated by the formation of excimers between Pyrene molecules covalently bound to Polyacrylic acid (PAA) within the film. At pH 3.8 the excimer/monomer ratio is higher than at pH 7.4 due to a lower PAA charge density leading to a stronger chain coiling at lower pH. At this pH the excimer/monomer ratio increases much stronger than at higher pH during the film formation which indicates a more pronounced condensation of the polymer segments. **(Fig. 2)**.

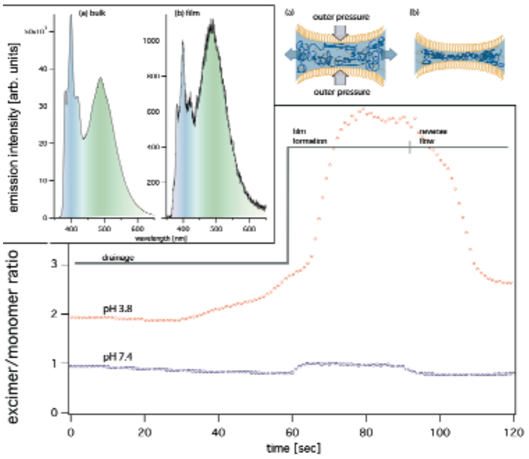

Fig. 2: Left hand side: Fluorescence spectrum of aqueous SDS/Py-PAA solution in the bulk phase and in a foam film. Right hand side: Excimer/Monomer ratio during the increase of the outer pressure (film formation) and pressure decrease (reverse flow) for two different pH.

This result correlates to the fact that at pH 7.4 an oscillating disjoining pressure occurs while its distance dependance is continuous at pH 3.8. The effect of *inter* and *intra*molecular interactions has been checked by different distribution of the dye labels.

Effect of Surface Modification

In all cases the *foam films* are stabilized by surfactant molecules well below the cmc. While the period of the pressure oscillations is independent of the surfactant used, the total thickness of the foam film can be tuned by the polyelectrolyte/surfactant combination. The addition of polyelectrolytes to a foam film containing like charged surfactants leads to an increase in film thickness due to an enhancement of electrostatic repulsion between the film surfaces. This avoids a transition from a thicker Common Black Film (CBF) to an ultrathin film (Newton Black Film, NBF, 4 nm thick). Qualitatively the same behaviour is observed for foam films containing polyanions and nonionic surfactant. If the polyanion is exchanged by polycation in the presence of nonionic surfactant the foam film shows a transition from a CBF to a NBF **[2]**. This leads to the conclusion that film surfaces containing nonionic surfactant are negatively charged. It is assumed that the charges are caused by unoccupied sites, i.e. the free air/water interface.

A negative net charge of the air/water interface has been also confirmed by force measurements in *wetting films*. For this purpose a TFPB is used and a solid substrate is attached to one film interface, resulting in an asymmetric film (air/water/substrate). Such (asymmetric) wetting films give the opportunity to measure the sign of surface charges at the air/water interface. The substrate surface was modified by the adsorption of polyelectrolytes of different charges. While a water film on top of a substrate coated with polycations is unstable, the water film becomes stable after the adsorption of an additional polyanion layer **(Fig. 3)**.

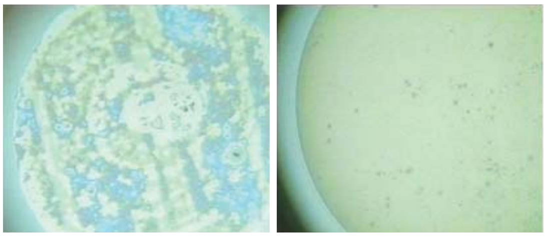

Fig. 3: Aqueous films on top of modified Silicon substrates: unstable on Si/ PEI (left), stable on Si/PEI/PSS (right).

The increase in ionic strength (by the addition of NaCl) leads to a decrease in film stability of former stable films, which proofs the dominating effect of electrostatic interaction on the film stability. Contact angle measurements showed that hydrophobic interactions can be excluded as reason for the film stability.

The origin of negative charges at the air/water interface is still unclear. Different models exist in the literature like the orientation of water and/or an excess of hydroxile ions at the air/water interface. In current experiments a) the sign of charge is varied by surfactants and water insoluble amphiphiles and b) ion specific effects are studied.

Polyelectrolyte Multilayers as Coatings

The substrate surfaces described above were modified by consecutive adsorption of oppositely charged polyelectrolyte. The investigation of polyelectrolyte multilayers presents an independent project in our group. We are concentrating on the effect of the degree of ionic strength and ion specific effects during the multilayer formation on the multilayer structure. The results show that beside inter- and intramolecular electrostatic interactions the gain in entropy and the specific interaction between polyelectrolytes and added small ions play an important role. After the formation has been finished the effect of environmental parameters like humidity, ionic strength and temperature has been checked. The swelling in vapour is most pronounced between a r.h. of 80 and 100% and it depends on the outermost polyelectrolyte layer **[3]**. The amount of water entrapped in the outer part of the film (ca. 100 Å) towards the vapour is much higher than in the inner part. This confirms results of former studies on diffusion of small molecules and neutron reflectivity indicating a more loosely packed structure of the outer part of the film. Increasing temperature leads to an annealing of the multilayers, but the incorporation of temperature sensitive polymers (e.g. PNIPAM) gives no additional swelling/shrinking. In order to check the influence of geometrical confinement on the volume transiton of PNIPAM, a current project deals with the formation of thermosensitive films of PNIPAM particles. The effect of the ionic strength depends strongly on the type of polyelectrolytes. For instance, PSS/PAH multilayers swell up to a NaCl concentration of 4 Mol/l **(Fig. 4a)**, while PSS/PDADMAC multilayers are destroyed at a NaCl concentration above 1 Mol/l **(Fig. 4b)**. In another current project the polyelectrolyte mobility of the polyelectrolyte chains is studied in dependence of the ionic strength, the type of salt and the degree of polymer charge.

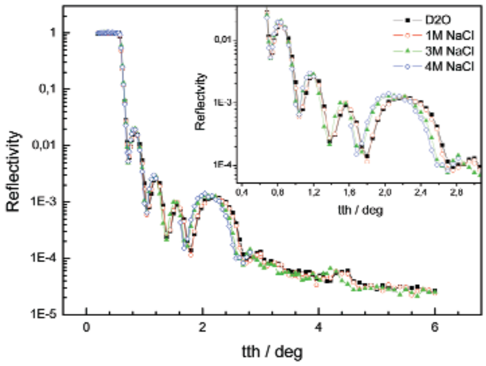

Fig. 4a) D_2O swollen PSS/PAH multilayer with a d-PSS superlattice at different outer ionic strengths (adjusted with NaCl) – in collaboration with Roland Steitz, HMI, Berlin

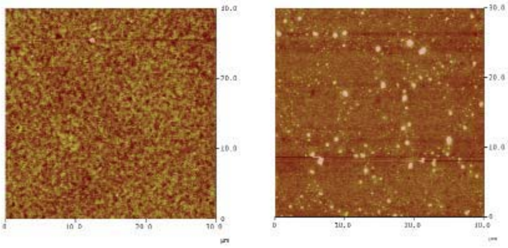

Fig. 4b) AFM micrographs of a PSS/PDADMAC multilayer exposed to 1 Mol/l (left) and to 2.5 Mol/l aqueous NaCl solutions (right).

Future Work

The question on the different packing properties of branched polyelectrolytes and Si particles within liquid films will be studied with particles of different deformability. Beside the studies of *statics*, i.e. force measurements in liquid films and investigation of the structure of adsorbed multilayers, future experiments will concentrate on the *dynamics*. This is for instance fluidics in thin liquid films and the mobility of the polyelectrolyte chains in liquid and adsorbed films. Thereby the fluid-"wall" interactions remain in the focus of interest.

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Key Publications:

[1] v. Klitzing, R., Kolaric, B.: Influence of polycation architecture on the oscillation pressure in liquidfree-standing films. Progr. Colloid Polym. Sci. **122**, 122-129 (2003).

[2] Kolaric, B., Jaeger, W., Hedicke, G., v. Klitzing, R.: Tuning of foam film thickness by different (poly)electrolyte/surfactant combinations. Phys. Chem. B **107**, 8152-157 (2003).

[3] Wong, J.E., Rehfeldt, F., Tanaka, M., v. Klitzing, R.: Swelling Behavior of Polyelectrolyte Multilayers in Saturated Water Vapor. Macromolecules **37**, 7285-7289 (2004).

Thermodynamics of Thin Layers

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Aims

We study changes in the thermodynamic properties of matter when it is confined in thin layers. In such layers the interaction forces between the surfaces come into action and some effects (e.g. disjoining pressure) which cannot be observed in the bulk systems appear. We studied experimentally two systems: 1) Very thin Newton black foam films (NBF) were used to understand the changes in the adsorption density of the surfactant molecules at the liquid/air interface when it is in close proximity of another surface; 2) Thin polyelectrolyte films on solid support were used to get information about the distribution of mobile components under the action of the surface interaction forces.

Results

Effect of the Applied Pressure on the Film Stability

We studied the stability of the thinnest NBF when pressure was applied on their surfaces. The experiments were performed using the *thin film pressure balance* (TFPB) technique. Although the thin foam films are thermodynamically unstable at certain conditions (e.g. high surfactant concentration) their stability is high enough and they can exist even for years. The NBF are the thinnest possible foam films. They consist of only two adsorption layers of the surfactant molecules adsorbed onto each other. Their properties (e.g. thickness) are invariable over a large range of thermodynamic conditions. The NBF rupture at certain critical pressure applied normal to their interfaces. The concept of *enhanced colloidal interaction* (ECI) in thin liquid films delivers an expression describing the dependence of the adsorption density at the film surfaces depending on the external pressure. On increase of the external pressure the surfactant density at the film surfaces decreases **(Fig 1a)**. At a certain critical value of the pressure the surfactant density is so low that a hole with a critical radius appears in the film. This hole grows spontaneously and the film ruptures **(Fig. 1b)**. Experiments were performed to determine the critical pressure for film rupture P_{crit} on variation of the concentration of surfactant in the solution used for film formation. The critical rupture pressure was measured for NBF formed from solutions of SDS in a wide range of surfactant concentrations and in presence of NaCl. The results are shown in **Fig. 1c**. The critical pressure increases on increasing surfactant concentration in the range below the cmc. It tends to a constant value at surfactant concentrations above the cmc. The full line in **Fig. 1c** shows the theoretical prediction according to our model. The theoretical calculations are based only on experimental data for the surface tension, the adsorption density at bulk solution interfaces, and the disjoining pressure in the film. No adjustable parameters are used to calculate the theoretical values. The theory prediction demonstrates reasonable correlation in the whole range of surfactant concentrations.

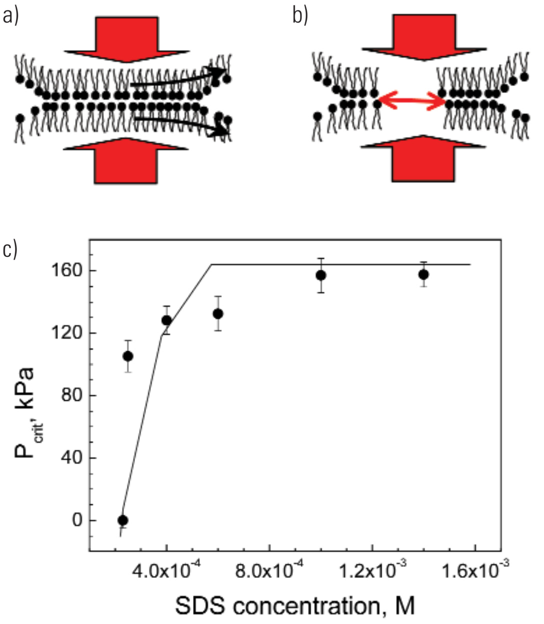

Fig. 1: a) Desorption of surfactant molecules from the NBF surfaces as a result of increased external pressure; b) NBF with formed critical hole which spontaneously grows and the film ruptures; c) Experimental data (●) and theoretical predictions for the critical rupture pressure as a function of the SDS concentration.

Effect of the Film Thickness on the Vapour Distribution in Thin Polyelectrolyte Films

The concentration of mobile components in nano-structured systems may depend on the dimension of the system. When two semi-infinite phases are separated by a thin layer the two interfaces interact with each other below a certain distance. This interaction leads to changes in the thickness of the thin layer, well described by the DLVO theory in the case of easily deformable (fluid) materials. In the case of stiff materials the film thickness cannot be changed, and the effect might lead to an exchange of mobile components between the thin layer and its surrounding. Such a dependence should appear, if the dimension of the system under consideration approaches the range of action of the the surface forces (less than 15nm). Then the chemical potential becomes a function of the dimensions and the concentration of a mobile component will change. We checked this hypothesis in the case of the absorption of water vapours in polyelectrolyte multilayers (PEM) with different thickness deposited onto solid support. The effect was studied by neutron reflectometry which gives information about the amount of water in the PEM as well as its distribution normal to the film interface. The amount of water in the PEM was calculated knowing the scattering length density of the material in dry and wet state. We observed a decrease in the water content upon increase of the number of PE layers **(Fig. 2)**. Only the first point in the dependence (PEM with one PE bilayer) deviates from the trend. This might be an effect of lower precision of determination of the SLD of that sample or its non-homogeneous structure which consists of many empty voids. The observed effect can be explained by the increased chemical potential of the water in very thin PE films which results in its desorption. This is one of the possible explanations. For detailed description of the observed behavior one has to keep in mind the changes in the bulk density of the PEMs when near to the solid support/PEM film interface. It might be also possible that the PEM film density depends on the number of adsorbed PE layers. If it increases with the increase of the PE layer number a similar effect might be observed.

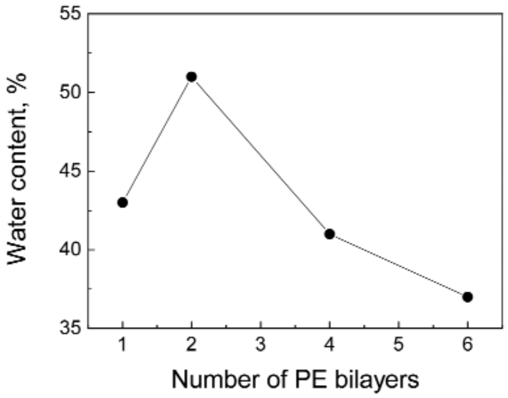

Fig. 2: Water content as a function of the number of PE bilayers

Future Work

The properties of wetting films will be studied in details. These films play an important role when a liquid flows near a solid interface. Thermodynamic description of the interactions in such films will be developed and their influence on the film stability will be studied. Complex fluids will be included in the experimental studies and their properties near an interface will be probed. Together with the classical methods used for studies of liquid films also neutron reflectometry will be applied. Investigations with bioactive compounds will be also performed. The procedures for formation of adsorbed layers with defined properties on solid support will be developed.

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Key Publications:

[1] Mishra, N.C., Muruganathan, R.M., Müller, H.-J. Krustev, R.: The dependence of the interactions in foam films on surfactant concentration. Colloids and Surfaces A **256**, 77-83 (2005).

[2] Mishra, N.C., Müller, H.-J., Krustev, R.: Mechanism for the rupture of foam film at higher external pressure. Proceedings International Symposium on Advanced Materials and Processing (ISAMAP-2K4). Indian Institute of Technology, Kharagpur, India, 195-202 (2004).

[3] Gutberlet, Th., Klösgen, B., Krastev, R., Steitz, R.: Neutron Reflectivity as Method to Study in-Situ Adsorption of Phospholipid Layers to Solid-Liquid Interfaces. Advanced Engineering Materials **6**, 832-836 (2004).

(QUASI) PLANAR INTERFACES – FLUID INTERFACES

Thermodynamics, Kinetics and Dilational Rheology of Interfacial Layers

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2002: Research Stay
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Aims

Non-equilibrium properties of interfacial layers are the most relevant characteristics for the control of many technical applications. Especially the understanding of foams and emulsions depends on the detailed knowledge of the dynamic and mechanical properties of the relevant interfacial layers. Moreover, a quantitative description of the adsorption dynamics and dilational rheology requires exact information on the interfacial thermodynamics.

The main target of the present work comprises experimental and theoretical work on the thermodynamics and non-equilibrium properties of interfacial layers built by proteins and protein-surfactant mixtures.

Thermodynamics of Adsorption Layers

In the framework of the two-dimensional non-ideal solution theory, the respective thermodynamic relationships were derived recently for surfactants, proteins and their mixtures, i.e. surface layer equations of state, adsorption isotherms. Also functions of the distribution of protein or surfactant molecules in respect to different molar area and the interfacial layer composition as a function of the bulk composition were derived. The basis for all thermodynamic models is the generalized Butler equation for the chemical potentials of the components, and a first-order model for the non-ideality of surface layer enthalpy and entropy.

The resulting equations satisfactorily describe measured adsorption and surface pressure isotherms of various systems. The new models allow the analysis of single component solutions, as well as mixed solutions, For example, the well-known differences between proteins and ordinary surfactants are reflected impressively: a sharp increase in the surface pressure with concentration beyond a certain protein adsorption, an almost constant surface pressure at higher concentrations and a significant increase in the adsorption layer thickness with increasing adsorption **(see Figs. 1 and 2)**. Also the differences between flexible (β-casein) and globular proteins (β-LG, BSA, HSA) are quantitatively described by the model, i.e. essentially by the molar area and its change with surface pressure. Note, with one and the same set of parameters (area per molecule, number of different interfacial configurations, surface activity), all different dependencies are reflected – $\Pi(c)$, $\Gamma(c)$, $\Pi(\Gamma)$ and others. This comprises various sets of experimental data, received not only from tensiometry but also from surface reflectivity and ellipsometry. Such experiments give direct access to the adsorbed amount $\Gamma(c)$.

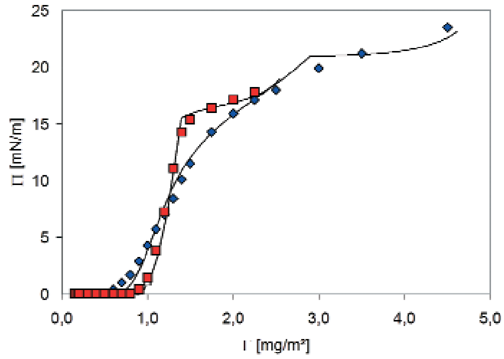

Fig. 1: Dependence of surface pressure Π on adsorption Γ, for β-casein (◆) and BSA (■), points are experimental data, curves calculated from the new model [1]

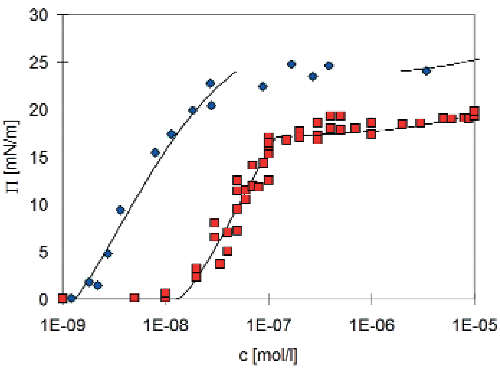

Fig. 2: Dependence of surface pressure Π on concentration c of β-casein (◆) and HSA (■), points are experimental data, curves calculated from the new model [1]

The **Fig. 3** illustrates the experimental surface tension isotherms for the globular human serum albumin (HSA), the non-ionic surfactant C_{10}DMPO and mixtures of HSA/C_{10}DMPO as a function of the surfactant concentration at a fixed protein concentration of 10^{-7}mol/l. The curves were calculated with the recently developed models for the single systems. Note, the models for the mixed systems used only characteristic parameters of the single components. We can see that the equilibrium adsorption of the protein mixed with the non-ionic surfactant C_{10}DMPO can be very well described. Similar results were obtained for other mixed systems, such as β-lactoglobulin mixed with C_{10}DMPO. Also mixtures of proteins with ionic surfactants (complex formation) are successfully studied, for example HSA/CTAB and β-LG/SDS.

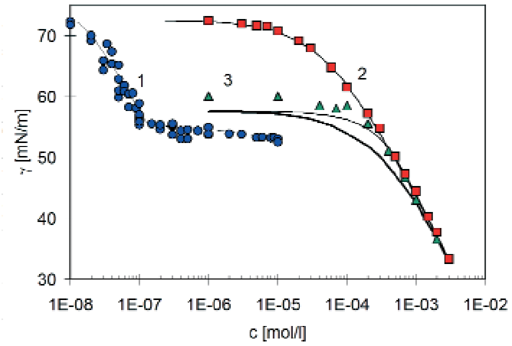

Fig. 3: Surface tension of HSA (●), C_{10}DMPO (■) and of mixed solutions of HSA (10^{-7}mol/l) with C_{10}DMPO (▲), points are experimental data from literature, curves calculated from the new model [2]

Adsorption Kinetics of Mixed Protein-Surfactant Adsorption Layers

Based on the advanced thermodynamic models, describing the equilibrium state of mixed adsorption layers, also the kinetics of adsorption from mixed solutions was investigated experimentally and respective theoretical models were developed.

Experimental dynamic surface tensions measured for solutions containing β-LG (10^{-6}mol/l) mixed with C_{10}DMPO are shown in **Fig. 4**.

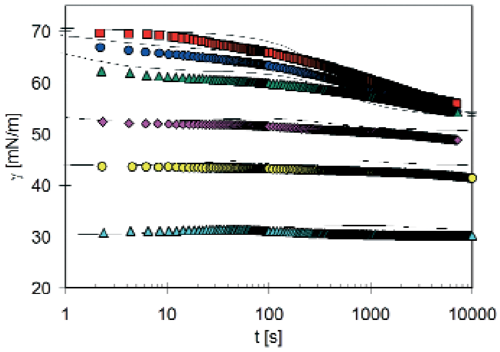

Fig. 4: Dynamic surface tension of a 10^{-6}mol/l β-LG solution mixed with C_{10}DMPO at different concentrations c = 0.01 (■); 0.04 (●); 0.1 (▲); 0.4 (◆); 1.0 (●); 4.0 (▲) mmol/l, points are experimental data from literature, curves calculated from the new model [2]

The data are in satisfactory agreement with the predictions made from the diffusion-controlled model. The equation of state and adsorption isotherms for the single components and the mixtures are used as boundary conditions. For the first time, a quantitative analysis of adsorption data for protein/surfactant mixtures was given.

Dilational Rheology of Protein Adsorption Layers

The dilational rheology represents a second independent access to the equilibrium and dynamic behaviour of interfacial layers, which is partly even more sensitive to particular properties, such as the structure of adsorbed species and the interaction in the adsorption layers. Values of the surface dilational elasticity and viscosity can be measured as a function of frequency, using different methods like harmonic and transient perturbations of the drop size, oscillating spherical drops and bubbles, and damping of capillary waves.

We found that the limiting elasticity for proteins, having a variable molar area, is lower than that characteristic for adsorbed molecules with constant area by the factor of $(1+d\ln\omega/d\ln\Gamma)$. For the flexible protein, β-casein, the dependence $\omega(\Gamma)$ is much stronger than for the globular protein, BSA.

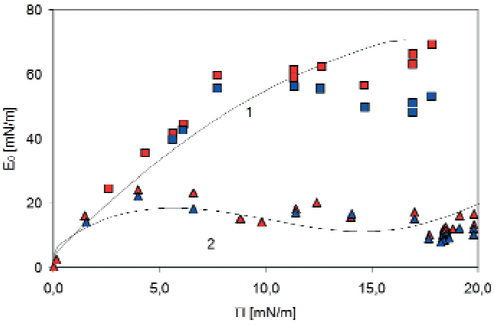

Fig. 5: Dependence of the limiting surface elasticity E_0 on the surface pressure, BSA (1) and β-casein (2), points are experiments for BSA at frequencies 0.084 (■) and 0.84 rad/s (■), and for β-casein at frequencies 0.033 (▲) and 0.84 rad/s (▲) [3]

A theoretical model proposed by Joos already in 1976 for the estimation of the limiting elasticity of mixed surfactant solutions, was modified by us such that it can be applied to mixtures of non-ionic surfactants and proteins. This model is again based on the parameters of the single compounds and describes the adsorption behaviour of the protein molecule in the mixed layer by accounting for its specific characteristics, such as the capability of folding and unfolding in the surface layer. In this context, the ability of the protein to decrease its molar area in a saturated monolayer can be considered in the presence of surfactant molecules.

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Key Publications:

[1] Fainerman, V.B., Lucassen-Reynders, E.H. and Miller, R.: Description of the adsorption behaviour of proteins at water/fluid interfaces in the framework of a two-dimensional solution model. Adv. Colloid Interface Sci. **106**, 237-259 (2003).

[2] Miller, R., Fainerman, V.B., Leser, M.E. and Michel, M.: Kinetics of adsorption of proteins and surfactants. Current Opinion in Colloid Interface Sci. **9**, 350-356 (2004).

[3] Lucassen-Reynders, E.H., Fainerman, V.B. and Miller, R.: Surface dilational modulus and Gibbs' elasticity of protein adsorption layers. J. Phys. Chem. **108**, 9173-9176 (2004).

Molecular Organization in Soluble Monolayers and Functional Films

Aims

We want to understand the static and dynamic properties of soluble amphiphiles at the air-water interface and its impact on macroscopic quantities. We utilize and further develop a variety of linear and nonlinear optical techniques to obtain a complete picture of the self-organization on a molecular scale.

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Results

Ion Distribution at Interfaces

The distribution of ions at a charged surface is a central problem of Colloid and Interface science. The classical approach is based on a mean-field approximation the prevailing ion distribution is determined by the competition between electrostatic interaction of point charges and thermal motion. Consequently, ions of the same valence should behave in the same fashion, which is in strong contradiction to the experiment.

Ion specific effects can be ordered in the so-called Hofmeister series. The diversity of effects is the result of a subtle balance of several competing evenly matched interactions. The complex interplay of electrostatics, dispersion forces, thermal motion, fluctuation, hydration and ion size effects and the interfacial water structure makes it hard or even impossible to identify a universal law. Consequently the list of decorations and modifications of the original Poisson-Boltzmann equation is long in order to provide a more realistic picture.

The decisive information is completely contained in the ion distribution at an interface. We developed a simple experimental protocol based on ellipsometry that provides insides in the prevailing ion distribution. The experimental data are interpreted in collaboration with Prof. Jungwirth, Prague. A highlight is the experimental proof of a counter ion condensation close to the cmc.

Surface Rheology and Foam Stability

The technique of an oscillating bubble allows the measurement of the complex surface dilational modulus of aqueous surfactant solutions. The principle is simple: Within a closed chamber a small hemispherical bubble is formed at the tip of a capillary (diameter 0.2 mm). The bubble is forced in a sinusoidal oscillation by a piezoelectric translator. As a result, a sinusoidal modulation of the pressure in the chamber is observed and evaluated. The experimental arrangement suppresses several unwanted effects such as a Marangoni flow and allows a sound modeling of the underlying processes. In collaboration with the group of Dieter Wantke we significantly improved the design of the apparatus. We are now able to measure with a high precision the complex surface dilational elasticity modulus of an aqueous surfactant system in an extended frequency range between 1 Hz and 1000 Hz.

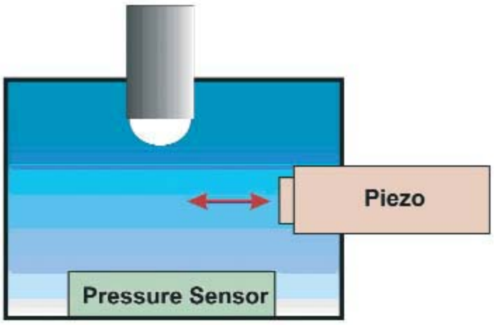

Fig. 1: Cross sectional view of the oscillating bubble device

The imaginary part of the modulus can be interpreted as an intrinsic surface dilational viscosity. Some surfactant systems are purely elastic while others exhibit a crossover to a surface visco-elastic behavior. Our data indicate that the existence of an intrinsic surface dilatational viscosity is a prerequisite for the ability of a surfactant system to form a stable foam lamella. Hence, we are able to link foam stability to a fundamental system parameter. The surface viscosity damps mechanical distortions of the foam lamella and thus prevents film rupture.

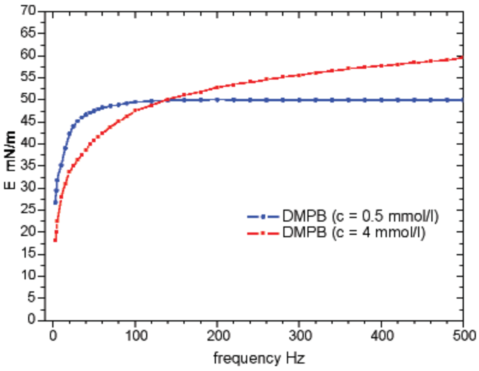

Fig. 2: Magnitude of the E-module for aqueous solution of DMPB

The upper figure shows the magnitude of the surface dilatational modulus at two different concentrations of our model system C_{12}-DMPB and the corresponding phase in **Fig. 3**. The model system shows a crossover between elastic and visco-elastic behavior with a slight increase of the bulk concentration. Only the visco-elastic system forms stable foam.

Furthermore we developed a novel oscillating bubble device system that monitors the nonequilibrium state with Surface Second Harmonic Generation. The data can be used to measure exchange rates and assess the surface rheological models of surfactant solutions. This project benefits from the close interaction with the group of Dieter Wantke.

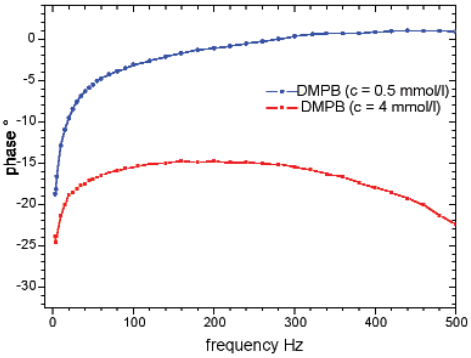

Fig. 3: Phase shift between piezo oscillation and measured pressure signal for aqueous solution of DMPB

Interfacial Water

Infrared–visible sum frequency generation (IR-VIS SFG) spectroscopy is a sophisticated and difficult to operate nonlinear optical technique that measures vibrational spectra of molecules at interfaces. The key feature is the inherent surface specificity. Only the interfacial species contribute to the spectra and not the bulk phases.

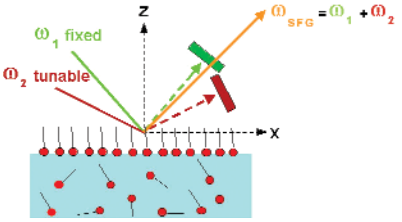

Fig. 4: Principle of IR-VIS sum frequency generation spectroscopy

IR-VIS-SFG can be used to probe the interfacial water structure. The IR-VIS SFG spectra of the amphiphile DMPB at two different concentrations is shown on the right hand side. The spectral region from 2800 to 3000 cm^{-1} can be attributed to CH stretching modes whereas the region from 3000-3800 cm^{-1} is dominated by the coupled and free OH stretching modes of interfacial water. The first prominent feature is an increase in the intensity of the bound OH stretching modes by a factor of ten as compared to the SFG spectra of pure water. This is the result of an increased probe depth due to the electrostatic field at the interface and an enhanced orientation of water molecules induced by this field.

The most surprising feature in the spectra is the fact, that the free OH peak is not present at the low concentration of DMPB (c = 0.5 mmol/l) whereas it is clearly detectable at higher concentrations (c = 4 mmol/l) just below the cmc. Keep in mind: pure water has a sharp free OH peak at 3700 cm^{-1}, this peak is missing at an intermediate concentration of the surfactant. Hence, the surfactant suppresses the free OH of water. Having this picture in mind it is obvious, that the revived free OH peak at higher concentration is the result of the exchange dynamics of the surfactants at the interface. In other words, the exchange of the surfactants causes the breaking of the hydrogen bonding network of water which costs energy. This dissipated energy is responsible for the existence of an intrinsic surface viscosity. This interpretation is consistent with the oscillating bubble experiments where only higher concentration shows a surface viscosity.

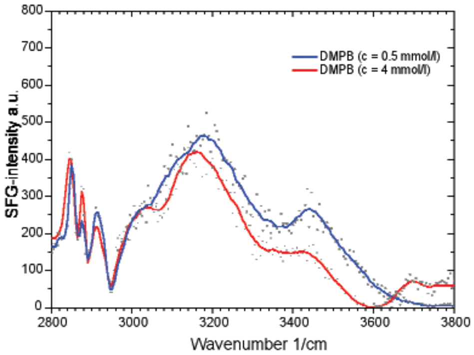

Fig.5: IR-VIS sum frequency spectra of DMPB of the interfacial water at two different surfactant concentrations

Surface Plasmon Spectroscopy

Surface plasmon resonance spectroscopy (SPR) is a widely used optical reflection technique for the characterization of the adsorption kinetics. The central quantity of SPR spectroscopy is the surface plasmon coupling angle as a characteristic signature of the prevailing interfacial architecture. Adsorption processes lead to a shift of the surface plasmon resonance, which is in the thin film limit directly proportional to the corresponding mass coverage. The aim of any SPR instrument is a precise measurement of the coupling angle with a sufficient high time resolution that fast kinetic processes can be monitored. We developed a novel scheme allowing to track the SPR minimum with an extremely high precison of 1/10.000 of a degree and a time resolution given by the electronics (50 Microsecods). This put us in the stage to investigate the early stages of surfactant and protein adsorption kinetics.

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Key Publications:

[1] Schneider, M., Andersen, A., Kölsch, P., Motschmann, H.: Following fast adsorption processes with surface plasmon spectroscopy: reflectivity versus mismatch tracking. Sensors & Actuators B-Chemical. **104** (2), 276-281 (2005).

[2] Kölsch, P., Motschmann, H.: A method for direct determination of the prevailing counterion distribution at a charged surface. Journal of Physical Chemistry B. **108** (48), 18659-18664 (2004).

[3] Örtegren, J., Wantke, K-D., Motschmann, H., Möhwald, H.: A study of kinetic molecular exchange processes in the medium frequency range by surface SHG on an oscillating bubble. Journal of Colloid & Interface Science. **279** (1), 266-276 (2004).

[4] Kölsch, P., Motschmann, H.: An experimental route to Hofmeister. Current Opinion in Colloid & Interface Science. **9** (1-2), 87-91 (2004).

Rheological Properties of Fluid Interfaces

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Aims

- Investigation of rheological properties of fluid interfaces and their influence on complex systems as foams and emulsions using mechanical and optical methods.
- Development of detailed molecular exchange mechanisms to explain rheological interfacial effects.
- Introduction of a framework for the general description of complex systems.

Results

Previous measurements of surface dilatational moduli of soluble surfactant solutions have exhibited a big discrepancy between experimental and theoretical curves. This effect was very often verified by the group using the oscillating bubble method and led to a discussion in the literature **(Fig.1)**.

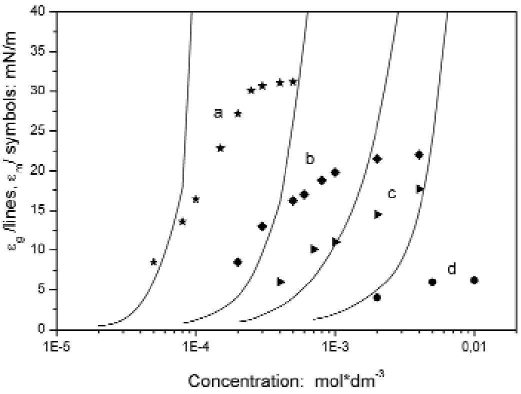

Fig. 1: Comparison between theoretical (line) and experimental Gibbs elasticities of n-nonanol (a), n-octanol (b), n-heptanol (c), and n-hexanol (d) solutions [1].

Its interpretation was also the main focus of the group during the last two years. An appropriate model should explain the measured effects, e.g. the intrinsic surface dilatational viscosity. Two alternative explanations are under discussion: a pure monolayer model and a model which takes into account the influence of the sublayer, too. The first model requires an overcompression near the saturation concentration of the surface during the compressing phase, whereas, in the second interpretation a molecular exchange between monolayer and sublayer is assumed. Then, the intrinsic viscosity can be interpreted as a dissipative loss due to this molecular exchange in a non-equilibrium state. The additional assumption of an enriched concentration in the sublayer explains the discrepancy between the experimental and theoretical results **[1]**. A related problem is the influence of this concentration on the static surface tension. Mechanical measurements in an equilibrium state are not suitable to verify such details of a surface model and independent experiments are required to support or refuse the interpretation.

For this reason two optical experiments were proposed and partially realized. In cooperation with the group of G. Brezesinski (M. Weygand) the complete surface excess concentration should be determined in a static state by SAXS-measurements. A first experiment exhibits significant differences between the results of SAXS-measurements using dodecyldimethylphosphine oxide solutions of approximately equal monolayer concentrations (determined with the aid of the equilibrium isotherm), however different bulk concentrations. This supports the hypothesis of an enriched sublayer concentration.

To verify the same point a SHG-experiment was realized in cooperation with the group of H. Motschmann (J. Örtegren). Using this equipment the actual monolayer concentration of a solution of a SHG-sensitive surfactant can be monitored at an oscillating bubble. **Fig. 2** shows the relative change in monolayer concentration normalized to the relative change of the bubble surface of fluortenside solutions.

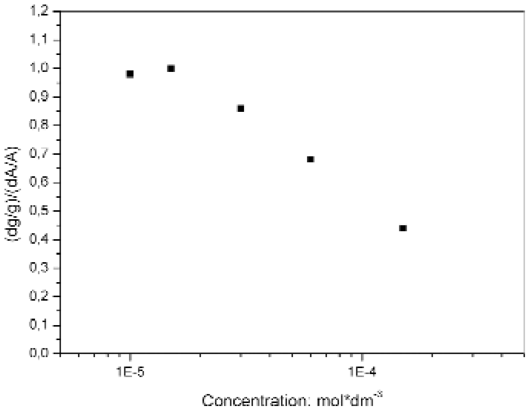

Fig. 2: The ratio of the relative change in surface concentration, dg/g, and the relative area change, dA/A, of a SGH-sensitive fluortenside solution during a fast bubble oscillation [2].

It demonstrates that for low concentrated solutions the dynamic surface tension is only a function of the actual monolayer concentration, whereas, in higher concentration ranges the molecular exchange with the sublayer must be taken into account **[2]**.

Further activities of the group were:

- studies of surface dilatational properties of mixtures **[3]**,
- modeling of results measured by chemical force microscopy in cooperation with P. Warzsynski/Krakau and G. Papastavrou/Genf, and
- investigations of foam systems in cooperation with the group of J. Ralston/Adelaide. The foam stability of special systems measured in Australia, were correlated with their surface rheological properties determined in the laboratory of our institute. The proposed hypothesis about the stabilizing effect of the intrinsic surface viscosity could be verified again.

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Key Publications:

[1] Wantke, K.-D., Örtegren, J., Fruhner, H., Andersen, A., Motschmann, H.: The influence of the sublayer on the surface dilatational modulus. Colloids Surf. A in press.

[2] Örtegren, J., Wantke, K.-D., Motschmann, H., Möhwald, H.: A study of kinetic molecular exchange processes in the medium frequency range by surface SHG on an oscillating bubble. J. Colloid Interface Sci. **279**, 266-276 (2004).

[3] Wantke, K.-D., Fruhner, H., Örtegren, J.: Surface dilatational properties of sodium dodecyl sulfate/dodecanol solutions. Colloids Surf. A **221**, 185-195 (2003).

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

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Aims

Long chain 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.). These processes are relevant for the early stages of solidification/melting (nucleation, cluster formation) as well as (non-equilibrium) bulk aggregation.

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?

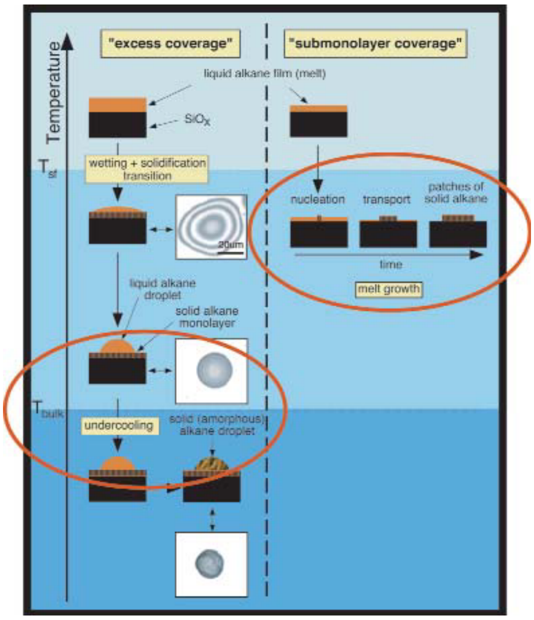

Fig. 1: Selection of topologies of alkanes at solid/gas interfaces (encircled are the regions of special interest to us).

Results

Molecularly thin films of long chain alkanes (e.g. $C_{30}H_{62}$) at solid/gas interfaces (e.g. SiO_2/air) show an amazing variety of different topologies (droplets, domains, films, layers, terraces) depending on the surface coverage, temperature, and preparation history. Three distinct temperature regions can be identified **(Fig. 1)**:

1.) In the high temperature range (light blue background) all alkane is molten and forms a completely wetting film of uniform thickness.
2.) In an intermediate range (medium blue), the alkanes adjacent to the solid surface solidify ("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.
3.) Below the bulk melting temperature, T_{bulk} (darker blue), all alkane is solid (in equilibrium).

Samples with "sub-monolayer coverage" are special because there is

1.) no "excess" alkane left for the wetting transition
2.) no coexistence of liquid droplets and frozen monolayer and,
3.) the "frozen" alkanes form 2-D domains

Currently we focus on nucleation, molecular mobility, and structure formation

1.) in the region of T_{sf} for sub-monolayer coverage
2.) around T_{bulk} for excess coverage.

In both cases the wetting/transport behavior and molecular flow is coupled to a liquid/solid transition.

For *sub-monolayer coverage*, upon solidification, the alkanes aggregate into domains with the molecules oriented upright at the interface in an alltrans conformation. **Fig. 2** shows an example of on-line observations of this nucleation-dewetting-aggregation process via optical interference enhanced optical microscopy (thickness contrast between domains and film < 4nm!). The domain density is determined by the (2D)-nucleation conditions. The temperature behavior agrees with classical nucleation theory (more domains at higher undercooling). The relation between coverage and nucleation is not yet understood. The domain shape is governed by solidification and lateral transport processes. During solidification the domain growth is supplied by the lateral flow/diffusion of mobile alkanes in the liquid film towards the solid domains. The domains have fractal shapes. At low surface coverage the dewetting-aggregation process is analogous to diffusion-limited aggregation (DLA), i.e., a quasi-2D-lateral alkane flow and with "hit-and-stick" of the molecules at the solidification front. At higher surface coverages (thicker liquid films), the lateral transport properties change from 3D to 2D upon drainage and the solid growth fronts come sufficiently close to interfere with each other. The process is much more complicated than "simple" DLA, the growth kinetics and the domain fractality change.

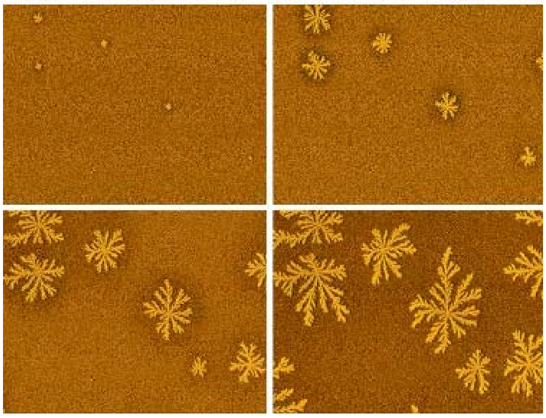

Fig. 2: Time sequence of microscopy frames showing a nucleation-dewetting-aggregation process. The bright fractal-shaped solid alkane domains are about 30Å thicker than the surrounding liquid alkane film (please note the depletion zone in front of the domains).

If a sample with *excess coverage* is cooled only slightly below bulk melting most droplets remain liquid, i.e. the liquid alkane bulk can be under-cooled. Instead of bulk solidification, the alkanes prefer to solidify into solid mono- and multilayer terraces with a center liquid droplet **(Fig. 3)**.

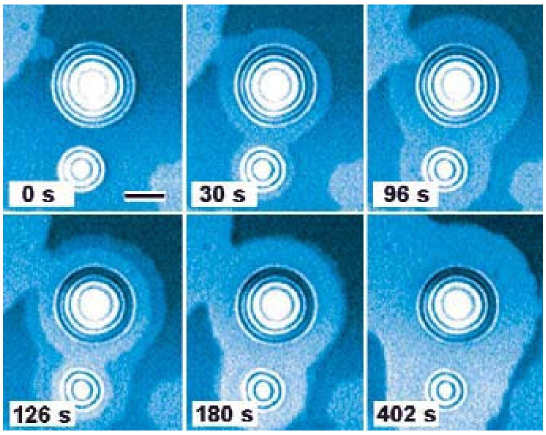

Fig. 3: Growth of solid mono/bi-layer terraces

The solid terraces grow radially with the liquid alkane of the center droplet serving as reservoir to supply the terrace growth via diffusive alkane flow on top of the solid terraces **(Fig. 4)**.

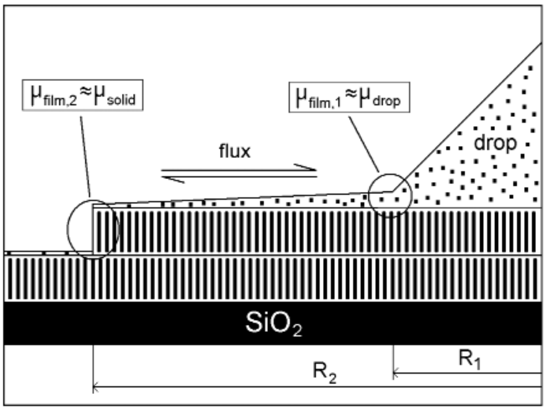

Fig. 4: Schematic of a cross-sectional cut through a growing monolayer terrace

The terrace growth is driven by the temperature-dependent chemical potential gradient between the under-cooled (non-equilibrium) droplet and the terrace edge **(Fig. 5)**. It is found that the entire sample surface is covered with a thin film ("precursor") of mobile alkanes. Chemical potential gradients between different sample sections induce alkane flow through this film.

The interaction between wetting, transport properties, and ordering transitions is quite spectacular in the case of heating the solid terraces above bulk melting.

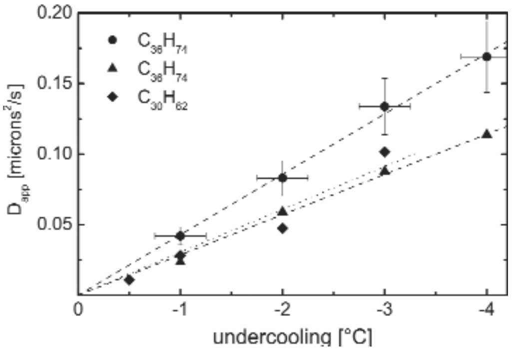

Fig. 5: Apparent diffusion constant as function of undercooling

Upon sufficient heating, droplets nucleate at the terrace perimeter and eventually start to move into the terrace area **(Fig. 6)**. While they move, they grow by melting and incorporating the solid layer sections ahead. The enthalpy of melting has been identified as driving energy for these "running droplets" (counterbalanced by viscous drag). By undercooling the movement can even be reversed.

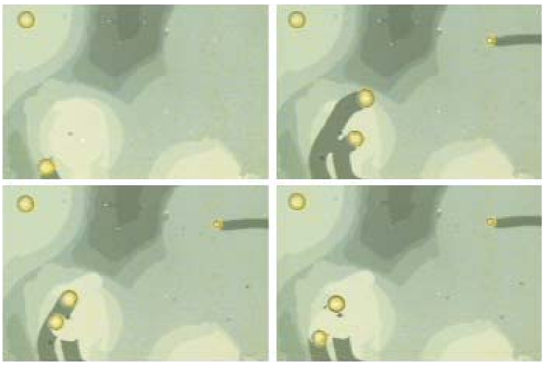

Fig. 6: Advancing (upper two frames, T>bulk melting) and receding (lower two frames, T<bulk melting) droplets

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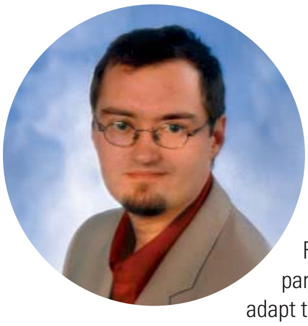
Key Publications:

[1] Schollmeyer, H., Struth, B. and Riegler, H.: Long chain n-alkanes at SiO_2/air-interfaces: Molecular ordering, annealing, and surface freezing of triacontane in the case of excess and submonolayer coverage. Langmuir **19**, 5042-5051 (2003).

[2] Knüfing, L., Schollmeyer, H., Riegler, H. and Mecke, K.: Fractal Analysis Methods for Solid Alkane Monolayer Domains at SiO_2/Air Interfaces. Langmuir, **21** (3), 992-1000 (2005).

[3] Lazar, P., Schollmeyer, H. and Riegler, H.: Spreading and two-dimensional mobility of long-chain alkanes at solid/gas interfaces. Phys. Rev. Lett. **94** (11), 116101 (2005).

Nanoscale Membranes: Adhesion and Mechanics



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Aims

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 membranes are far from being so "smart", but in recent years tremendous progress has been made in their production and a major goal is to create artificial systems that possess stimuli responsiveness or specific interactions like the natural examples: Our aim is to explore novel routes for the design of such structures and to provide tools for studying their mechanical and adhesion properties. This is the prerequisite for gaining understanding of how membranes can be tailored or even be made responsive in their mechanics or interactions. In particular we are interested in nonfluid membrane systems, like polymeric membranes or membranes formed by interfacial nanoparticle assembly.

Results

Membrane Mechanics: Force Spectroscopy of Capsules and Flat Membranes

AFM provides an excellent tool to study the mechanical properties of ultra-thin membranes, since nanoscale deformations can be applied and a force range between 10s of piko-N up to a micro-N is accessible. At the same time, the lateral position of the force probe can be controlled with nm precision such that also small membrane objects like micro- or nanocapsules can be probed.

We have applied colloidal probe AFM in combination with optical techniques **[1]** 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. The technique is suitable for a broad range of capsule systems and was so far used for studying the mechanical properties of polyelectrolyte multilayer capsules (PEC) and crosslinked pickering emulsion systems (CPE).

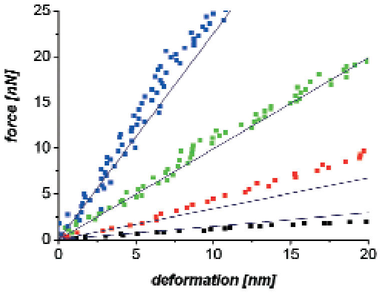

Fig. 1: Force versus deformation data for capsules of radius between 2 and 5 microns and wall thickness between 20 and 60 nm. Wall thickness and radius allow adjusting the capsule compliance over a large range, the solid lines are theoretical predictions based on continuum mechanics assuming a constant elastic modulus for all capsules.

Fig. 1 shows an example of force deformation data of PECs of different radii and wall thickness. Both parameters can be precisely controlled and varied over a large range giving rise to large differences in the capsule stiffness. Our results show that the majority of PECs are formed from polymers in a glassy state, which also explains the robustness of these systems. Interestingly, transitions from glassy to elastomeric state can be induced by changing solvent parameters, like in the example shown in **Fig. 2** the salt concentration in the aqueous medium **[2]**. These changes can be studied in situ and show an example of stimuli responsiveness that is found in these systems.

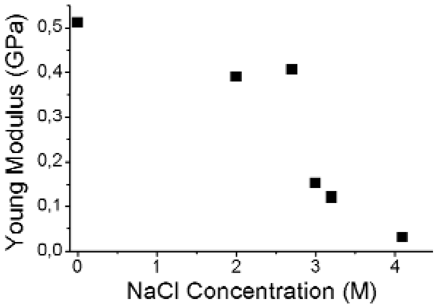

Fig. 2: Dependency of the Young modulus of polyelectrolyte capsules on the salt concentration derived from capsule deformability measurements.

The second system CPEs are based on Pickering emulsions: Pickering emulsions are formed when in a binary liquid system (e.g. oil in water), nanoparticles are introduced that have a wettability which favors nanoparticle self-assembly at the oil water interface. The nanoparticles can subsequently be crosslinked forming membranes/capsules (CPEs). The instrumentation that was tested and developed for the PECs can be applied for the CPEs too, since the deformabilities are in the same range. In terms of physical properties, CPEs are very different from PECs, since here not only membrane elasticity but also surface tension plays a major role. By using different cross-linking strategies, the relative importance of these two contributions can be varied and studied.

The strategies to form PECs and CPEs can be modified such that flat membranes can be made. We have developed techniques for handling these ultra-thin films and make them freestanding. Techniques like bulge tests can be used to quantify their mechanics which can contribute to a better understanding of the more complex capsule systems. These systems might as well find applications as micron sized osmotic pressure sensors.

Membrane Adhesion: From Basic Understanding to Patterning

The adhesive properties of capsules and other membrane constructs are crucial for coupling these structures to surfaces and also for their mutual interactions.

We have studied the adhesion of capsules on homogeneous surfaces by reflection contrast interference microscopy (**Fig. 3** shows a typical RICM image from which the shape of adhering capsules can be reconstructed).

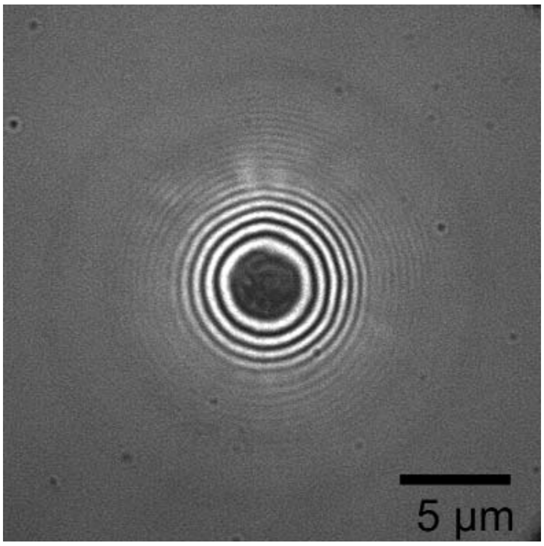

Fig. 3: RICM micrograph of an adhering capsule. The fringes correspond to the non contact regions close to the adhesion area (circular greyish area in the middle). The capsule shape can be reconstructed from the interferences.

We could demonstrate that the PEC system allows control of the size of adhesion areas by varying the capsule compliance: The compliance can be set by the thickness of the multilayer wall constituting the PEC membrane, while the interactions are determined by the polymer terminating the multilayer. Both parameters can be varied largely independent from each other and we have achieved a semi-quantitative understanding of the impact of those parameters on the adhesion process from these studies. In particular, these studies help to understand how the compliance of capsules can be designed such that different shape changes are triggered by adhesion (adhesion can result in shape changes to a truncated sphere geometry or even collapse of the capsule). Currently we are exploring the adhesion of capsules interacting with surfaces via specific (receptor-ligand type) interactions. Such systems can be relevant for drug delivery and form biomimetic model systems for cell adhesion.

If not homogenous surfaces but patterned ones are used, PECs can be self assembled into patterns **[3]**. For systems in which electrostatic interactions are dominating, this is achieved if capsules are exposed to surfaces which are patterned in their surface charge density possessing positively and negatively charged regions, although the concept is not limited to any particular kind of interaction. **Fig. 4** shows an example of self assembly of filled capsules on such a patterned surface. Especially if filled capsules are used, ordering on a surface is a first step towards sensor or reaction-container arrays on the micron scale.

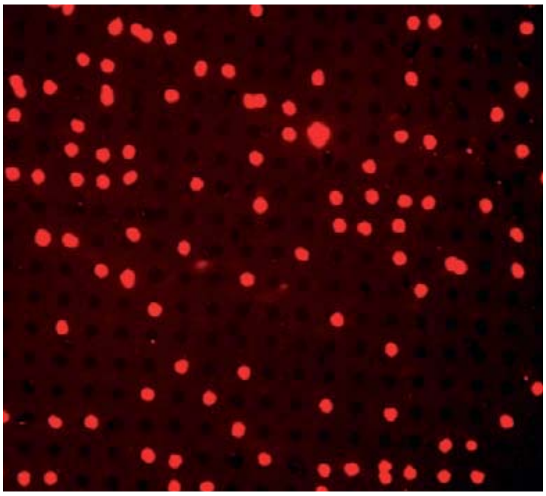

Fig. 4: Selective deposition of PECs on structured surfaces. The structure was printed with weakly labelled positively charged polyelectrolyte, while the positively charged PECs were strongly labelled; thus structure and shells are visible in the fluorescence image. The capsules are preferentially adsorbing to the non printed areas that are exposing the oppositely charged PSS.

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Key Publications:

[1] Dubreuil, F., Elsner, N. and Fery, A.: Elastic properties of polyelectrolyte capsules studied by atomic force microscopy and RICM. Europhys. J. E **12** (2), 215-221 (2003).
[2] Heuvingh, J., Zappa, M. and Fery, A.: Salt induced softening transition of polyelectrolyte multilayer capsules. Langmuir, in press, (2005).
[3] Nolte, M. and Fery, A.: Coupling of individual polyelectrolyte capsules onto patterned substrates. Langmuir, **20** (8), 2995-2998 (2004).

NON-PLANAR INTERFACES

Modular Materials: From Dynamic to Nanotechnological Devices

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Since 4/2004: Director, Functional Modules Group (National Institute for Materials Science, Tsukuba, Japan)

Aims

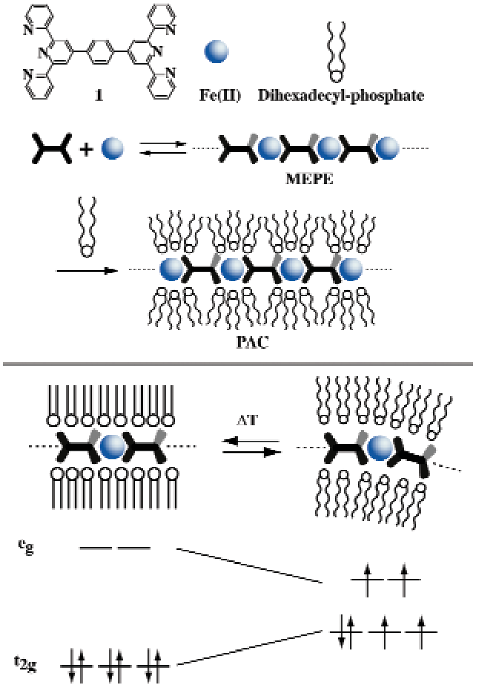
Metallo-supramolecular modules are at the focus of materials research for the construction of functional devices for sensing, transformation (catalysis), and signal transduction. The increasing importance of MEMOs rests on the fact that self-assembly of metal ions and ligands provides an elegant and efficient access to a plethora of well-defined structures and value-adding functions. Our research concerns all aspects of molecular self-organization to fabricate various architectures, including nanostructures, mono-layers, thin films, as well as mesophases. Our research embraces all aspects of structure and property examination in order to establish structure-property relationships of the materials. Two classes of components are relevant for our work, namely extended metallo-supramolecular assemblies and discrete polyoxometalate clusters (POM). These components possess a wide range of structural and functional properties (electrochemistry, photochemistry, catalysis, magnetism) that make them potential components for displays, sensors, separation, catalysis, electro-optic and magnetic devices.

Results

A. Metallo-Supramolecular Modules (MEMOs)

Ditopic ligands based on terpyridine receptors self-assemble with transition metal ions, such as Fe(II), Ni(II), or Co(II), to metallo-supramolecular polyelectrolytes (MEPEs). The molar mass of MEPE, investigated by analytical ultracentrifugation, is a function of concentration, solvent and pH. In the case of Ni(II) the highest detectable molar mass exceeds 350.000 g/mol indicating a high binding affinity of the ligand and Ni(II). The solid-state structure of Fe(II)-MEPE was characterized using electron diffraction techniques demonstrating that MEPE forms straight rods that are packed into sheets.

The positive charge of MEPE can be utilized in many ways for sequential self-assembly. Using the electrostatic layer-by-layer self-assembly (ELSA) protocol MEPE are readily incorporated into multilayers. Utilizing electrostatic interactions it is also possible to assemble MEPE and negatively charged amphiphiles, which results in formation of metallo-supramolecular polyelectrolyte-amphiphile complexes (PACs). Using a combination of small- and wide-angle X-ray scattering and molecular modeling we could refine the structure of the PAC mesophase down to nanoscopic levels. At room temperature, the hierarchical architecture comprises alternating lamellae of metallo-supramolecular polyelectrolytes and single, interdigitated amphiphile strata. Also, PACs form homogeneous monolayers at the air-water interface, which can be transferred onto solid supports using the Langmuir-Blodgett approach. These highly ordered multilayers are anisotropic. Using atomic force microscopy, we show that adsorption of PAC and alkanes on the basal plane of graphite yield perfectly straight PAC rods of nanoscopic dimensions.



Top: Sequential self-assembly of ditopic ligands, metal ions and amphiphiles results in a polyelectrolyte-amphiphile complex (PAC). Bottom: The temperature induced phase transition in the amphiphilic matrix results in a distortion of the coordination geometry, giving rise to a reversible spin transition of the Fe^{II} *ion.*

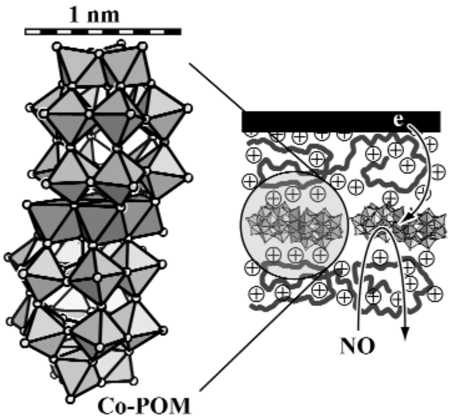
The occurrence of semi-occupied d-orbitals is responsible for some of the most prominent properties: The splitting of the d-orbitals in a ligand field of appropriate symmetry and strength can give rise to thermally or photo-induced spin transitions and spin crossover phenomena. The conversion between a low-spin (LS) and high-spin (HS) state is typically observed in transition metal ion compounds with a $3d^n$ ($4 \leq n \leq 7$) electronic configuration, the most extensively studied element being the FeII ion. In a ligand field of octahedral symmetry, the d-orbitals split in low-lying t_{2g} and high-lying e_g subsets. In the case of the Fe^{II} ion, the LS state arises from a closed-shell t_{2g}^6 electronic configuration and the HS state from a $t_{2g}^4 e_g^2$ electronic configuration, respectively. Spin crossover is generally accompanied by a change in the optical and magnetic properties.

As expected, the Fe(II)-PAC is diamagnetic due to the strong ligand field splitting induced by the coordination of the terpyridine units. However, heating these PACs results in an amphiphilic phase transition, which results in a distortion of the coordination geometry. In turn, the ligand field stabilization is reduced giving rise to a paramagnetic high-spin center. Upon cooling, the amphiphilic phase and the metal coordination center reassemble resulting in a reversible spin transition.

B. Polyoxometalate Clusters (POMs)

The ELSA method was applied to incorporate negatively charged POMs into thin multilayers. Through experimental conditions during deposition, we can tailor the surface coverage of POMs, as well as their electrochemical properties, and the permeability of the mutlilayers. The electrochemical properties of the POM-cluster are fully maintained in the ELSA films.

We fabricated a long-lived, selective, and sensitive NO detection sensor based on a POM as electro-catalytic sensitizer. Herein, we choose a cobalt(II)-substituted sandwich complex of formula $[Co^{II}_4(H_2O)_2P_4W_{30}O_{112}]^{16-}$ derived from the well-known Wells-Dawson anion α-$[P_2W_{18}O_{62}]^{6-}$. This POM cluster appears particularly promising for NO detection because Co(II) is known for its high affinity to NO. In addition, Co-POM has suitable redox potentials with respect to NO to provide rapid electron transfer.



Scheme of an electro-catalytic NO-sensor based on a polyoxometallate embedded in a polyelectrolyte matrix.

NO sensing is possible at concentrations as low as 1 nM and within a concentration window ranging from 10^{-9} to 10^{-5} M. Notably the sensitivity and selectivity can be adjusted through the multilayer architecture. The fact that no external electron-transfer mediators are required is particularly attractive.

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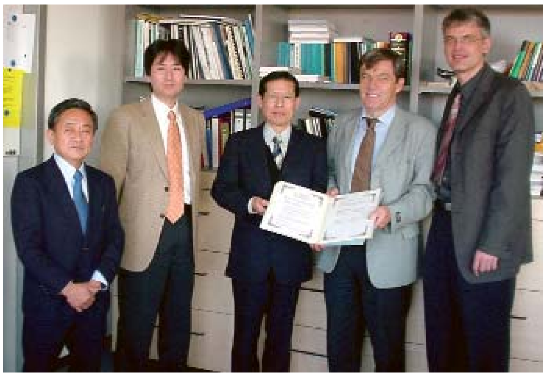
Functional Modules Group

Since April 2003, the MPI and the NIMS operate an international German-Japanese laboratory under the direction of D. G. Kurth. NIMS was founded three years ago as a result of a scientific and administrative reorganization of several scientific centers in Tsukuba, Japan. Now, NIMS pursues a vigorous program towards creating an international center of excellence. While NIMS has a strong background in solid-state materials, NIMS plans to broaden its scientific and technological expertise in new fields, such as soft matter. As a first initiative, NIMS has appointed the first foreigner as Director. The so-called Functional Modules Group is part of the Advanced Materials Laboratory (AML) and has been allocated a budget of approx. 1.8 Mill. EUR for three years. Each year, Kurth will spend 40 days at NIMS. Likewise, researchers from NIMS will come for 40 days each year to MPI. On the other hand, it is a unique opportunity for the MPI to participate in a close international collaboration under the framework provided by the Memorandum of Understanding signed by both parties.

The laboratory at MPI has focused mainly on the characterization of supramolecular architectures. The principles and methodologies developed so far will now be extended towards more complex systems. A central objective of the laboratory at NIMS is therefore the synthesis of novel molecular modules, which include terpyridine-based ligands with unusual substitution patterns or dendritically branched amphiphiles. Organic synthesis is therefore a main focus of the NIMS laboratory both in terms of human resources as well as scientific infrastructure. In a joint effort, the self-assembly of these units, the structure as well as the properties of the resulting architectures will be investigated. A frequent exchange of researchers from both sides has therefore become an integral part of this program in order to exchange expertise and to conduct experiments.



Signing the Memorandum of Understanding between MPI and NIMS. From left to right: Dr. Kamo (Vice President), Dr. Ichinose (Director), Dr. Watanabe (Director General), Prof. Möhwald (Director), Dr. Kurth (Project Leader, Director).

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Key Publications:

[1] Kurth, D.G., Pietsch, U., Bodenthin, Y., Möhwald, H.: Inducing spin cross-over in metallo-supramolecular polyelectrolytes through an amphiphilic phase transition. J. Am. Chem. Soc. accepted.

[2] Liu, S., Volkmer, D., Kurth, D.G.: Smart Polyoxometalate-Based Nitrogen Monoxide Sensors. Anal. Chem. **76**, 4579 (2004) .

[3] Severin, N., Rabe, J.P., Kurth, D. G.: Fully extended polyelectrolyte-amphiphile complexes adsorbed on graphite. J. Am. Chem. Soc. **126**, 3696 (2004).

NON-PLANAR INTERFACES

Bioinspired Control of Electrical and Optical Properties of Interfaces

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Since 1995: Professor,
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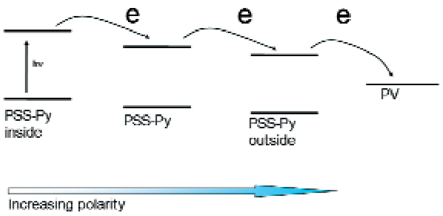
Aims

In natural photosynthesis light is funneled towards a reaction center via a specific arrangement of protein bound chromophores. Then charges are separated and transferred across a membrane where on both sides the electrical energy is converted into chemical energy. Objective of this project is to mimic some of these processes in a synthetic system with the long-range aim to assemble them in a system converting efficiently photon energy into electricity, chemical energy or into information.

The focus of the last two years concerned vectorial electron transfer, the basic idea being that the polarization energy of a charged state depends on the polarity of the environment. Hence in a material with polarity gradient an electron would move between the same molecules towards the higher polarity region **(Scheme 1)**.



Scheme 1: Energy levels of the pyrene anionic (top) and cationic (bottom) states and that of the polyviologen (PV)

Results

- It was previously shown that films with polarity gradient can be built by consecutive adsorption of oppositely charged polyelectrolytes. We coupled pyrene chromophores at polystyrenesulfonic acid (PSS-Py) in a molar ratio as high as 1:30 to achieve a rather high chromophore density.
- If one finally wants to obtain electrical energy, the film on a planar electrode would be preferred. However, if one wants to study the process by transient absorption spectroscopy the arrangement on a colloidal particle is needed. To minimize light scattering the optimum arrangement was in hollow capsules of ~0.5µm diameter. This system is also suited to convert inside and outside electrical into chemical energy in analogy to processes in chloroplasts.
- Building a film without polarity gradient the fluorescence of pyrene dispersed in the film can be completely quenched by adding a polymeric electron acceptor (polyviologen) on one side. Since energy transfer can be largely excluded this indicates electron transfer across the whole film **(Fig. 1)**.

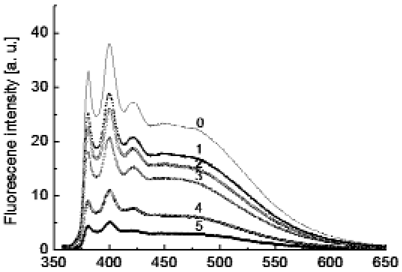


Fig.1a: Fluorescence spectrum of PSS-Py on adding increasing amounts (0-5) of the acceptor PV and for the film composition of Fig. 1b

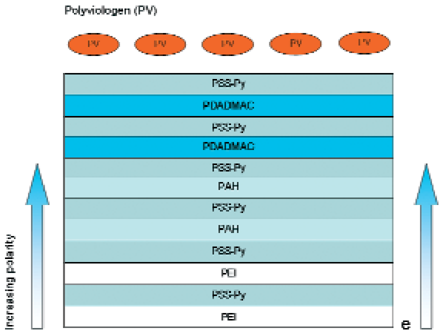


Fig.1b: Film design with PSS-Py in each anionic layer and with different polycations effecting a polarity gradient

- To reject a hypothesis of acceptor diffusion into the film a system was prepared by an "electron insulating" layer in the center exhibiting no pyrene. As expected, fluorescence could be quenched only by 50% **(Fig. 2)**

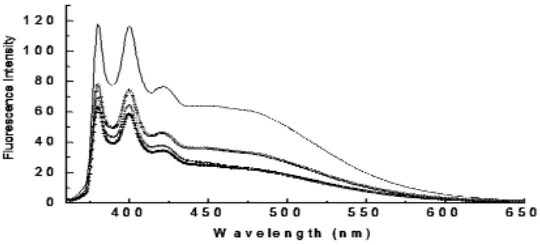


Fig. 2a: Fluorescence spectrum of PSS-Py with increasing acceptor concentration (top to bottom) for the film composition of Fig. 1b. Due to the insulating middle PSS layer the emission can not be decreased further by more PV addition

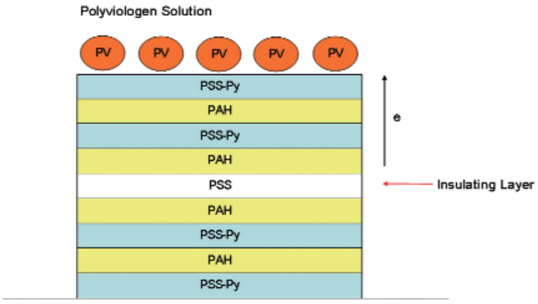


Fig. 2b: Film design with a middle PSS layer without Py coupled (insulating layer)

- Varying the chromophore density in this insulating layer a threshold density for efficient electron transfer could be derived. From this an average pyrene distance of 3.0 nm for efficient electron transfer could be calculated under the assumption of statistical dye distribution.
- Building a film with polarity gradient the threshold for efficient electron transfer could be reduced by 15%. This demonstrates the possibility of vectorial electron transfer by a polarity gradient **(Fig. 3)**

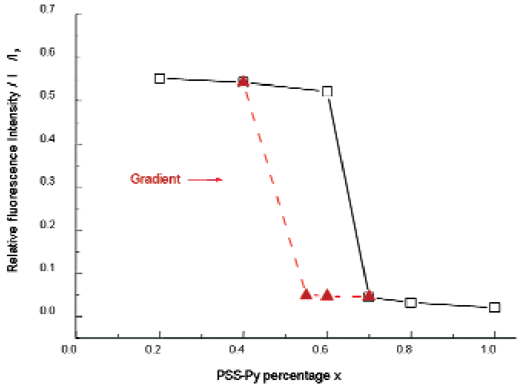


Fig. 3: Fluorescence intensity at maximum quenching (highest PV concentration) varying the PSS-Py/PSS ratio in the middle layer for the geometry of Fig. 2b (black squares) or for an analogous geometry but with a polarity gradient prepared as sketched in Fig. 1b (red triangles)

- The lifetime of the pyrene cation state could be increased by a polarity gradient from below 1µsec to about 50 µsec. This again indicates that the concept of charge separation via gradients seems to hold.

Future Work

Efficient electron transfer across distances of 3 nm is difficult to understand. One possible explanation is that the π-electrons of the styrenes in the film, although high in energy, mediate the coupling between pyrenes (superexchange). This calls for experiments with films where all polyelectrolytes possess no conjugated bonds.

- Lifetimes of intermediate states have to be measured quantitatively and systematically to understand the mechanism – Cooperation Prof. Menzel, University Potsdam
- Study analogous processes with systems closer to the biological one (porphyrins) – Cooperation Prof. Roeder, Humboldt University Berlin
- Couple electron transfer with a chemical reaction
- Study mechanism of charge injection into electrodes from dyes and proteins in different polyelectrolyte matrices – Cooperation Prof. Hildebrandt, Technical University Berlin

As a new direction now appears at the horizon the system of nanoparticles (CdTe, Au) containing dye functionalized polymer brushes. This should be investigated as a promising light harvesting system.

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Key Publications:

[1] Li, L., Tedeschi, C., Möhwald, H.: Synthesis of a Pyrene-labeled Polyanion and Its Adsorption onto Polyelectrolyte Hollow Capsules Functionalized for Electron Transfer. Chem. of Mat. **16**, 570-573 (2004).

[2] Tedeschi, C., Li, L., Möhwald, H., Kirstein, S., Menzel, R., v. Seggern, D., Spitz, C.: Engineering of Layer-by-Layer Coated Capsules with the Prospect of Materials for Efficient and Directed Electron Transfer. J. Am. Chem. Soc. **126**, 3218-3227 (2004).

[3] Li, L., Möhwald, H.: Photoinduced vectorial charge transfer across walls of hollow microcapsules. Angew. Chem. **43**, 360-363 (2004).

NON-PLANAR INTERFACES

Multifunctional Polyelectrolyte-based Micro- and Nanocapsules

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Aims

- Stimuli-responsive capsules for controlled encapsulation and release of chemical compounds
- Nanoreactions in restricted volumes)
- Development and application of capsules as Tools for detection, controlled delivery and site specific manipulation in vivo studies.
- Modification of the polyelectrolyte shell in order to impart new properties such as catalytic activity, magnetic or spectral sensitivity, electric conductivity, extremely low permeability, and enhanced protection ability against oxidation.

Results

Stimuli-Responsive Capsules as Microsensors and Microreactors:

Smart materials that can undergo sharp physical or chemical modifications under external stimuli were chosen for the engineering of polyelectrolyte microcapsules.

Thermosensitive capsules were prepared by incorporating PNIPAM inside $(PAH/PSS)_n$ hollow microcapsules. The polymer was synthesized using a "ship in a bottle" method and capsules loaded with PNIPAM were obtained. Observations by CLSM at variable temperature showed the encapsulated PNIPAM reversibly collapsing (insoluble particles) above 33°C (LCST). Electrolytes were used to shift this LCST and it depends on the nature of the ions used.

Response to pH was achieved by using weak polyelectrolytes. $(PSS/PAH)_n$ microcapsules templated on PS cores can be reversibly swollen at pH>11.5 where the PAH gets almost completely deprotonated. Electrostatic repulsions between the remaining negative charges of the PSS chains, as well as the effect of counter-ions seem to be responsible for this effect. Decreasing further the pH leads to shrunk capsules. The THF used during dissolution of the core is responsible for the increased stability of the swollen state (dissolution of the capsule is strongly slowed down). Another way to stabilize the system is the use of hydrophobic interactions present in weak polyelectrolytes such as PMA and PVP. Capsules made only of weak polyelectrolytes were prepared that can respond in both the acidic and the alkaline regions, depending on the apparent pKa of the polymers within the multilayers. $(PAH/PMA)_n$ and $(PVP/PMA)_n$ microcapsules change in size and morphology when one of the polyelectrolytes gets almost completely uncharged.

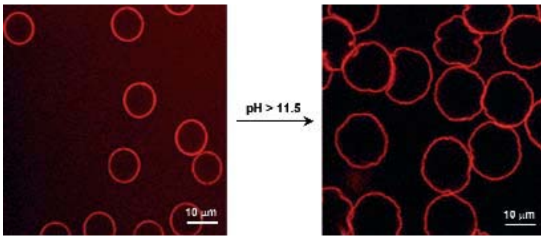

Fig. 1: Swelling of $(PAH/PSS)_n$ capsules in alkaline conditions

The reversible swelling of the pH-sensitive hollow microcapsules is accompanied by a dramatic increase in their permeability and was used to encapsulated polyanions inside $(PSS/PAH)_n$ capsules at high pH. After swelling and diffusion of the surrounding polymer, reducing the pH closes the pores and the polyanion gets encapsulated. The flexibility of this method allows a subsequent release of the material, by increasing again the pH. This property was used to determine the amount of encapsulated PAA that was found to be as high as 5pg per capsule. These systems were successfully used as microreactors: an insoluble complex between PAA and Ca^{2+}, reversibly formed as a function of the pH, was observed only in the interior of the capsules.

Polyelectrolyte Capsules as Protective Microcontainers:

Composite polyelectrolyte capsules protecting encapsulated material against oxidation are demonstrated: "passive" protective capsules composed of a sacrificial reducing agent as a shell constituent and "active" protective capsules including the catalyst for the decomposition of oxidative species deposited onto the shell as the outer layer. In the latter case, the protective material is not consumed thus prolonging the protection activity of the microcapsule. The designed microcontainers combine protective function with controlled release of the encapsulated material.

Nanosynthesis in the Capsule Volume:

Fluorescent rare earth nanophosphates, magnetite, hydroxyapatite, rare earth fluorides, metal oxides were synthesized inside hollow polyelectrolyte capsules without additional thermal treatment. The resulting nanoparticles are highly crystalline with the size ranging between 4-15 nm exhibiting, when relevant, fluorescence, magnetic or semiconductor properties. Inorganic nanoscaffold modifies the shell of the polyelectrolyte capsules increasing its stiffness and chemical stability. Composite inorganic/polyelectrolyte capsules can be used as delivery microcontainers in dried state.

Metallized capsules are obtained taking the initial capsules as template microreactor. Depending on the synthetic route, metallic capsules contain metal nanoparticles either only in the shell or both in the shell and capsule volume. The metallized capsules are of interest in optical and magnetic devices, as micronsized catalysts containing nanostructured active material, and as delivery microcontainers with a shell sensitive to electromagnetic radiation.

Temperature Treatment of Polyelectrolyte Capsules:

Polyelectrolyte capsules with even number of layers preserve their integrity after heating up to 120 °C in aqueous solution but show a considerable decrease in size (~70 % in diameter). A strong increase of layer thickness, which accompanies the diameter decrease, is enough to drastically reduce capsule permeability for ions and small molecules. The driving force for such a polyelectrolyte rearrangement process is the entropy gain through the more coiled state of the polyions and the decreased interface between polyelectrolyte shell and water. The heat treated capsules remain spherical upon drying **(Fig. 2)**.

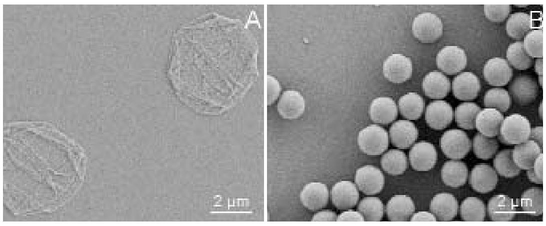

Fig. 2: Scanning electron microscopy images of dried (PSS/PAH)$_5$ polyelectrolyte capsules before (A) and after (B) incubation at 120 °C for 20 minutes

Remote Activation of Capsules by Laser Light:

A novel method for remote release of encapsulated materials from polyelectrolyte capsules based on laser light illumination was developed. Various components were introduced in the polyelectrolyte shells of PAH/PSS capsules - including inorganic materials like metal nanoparticles or organic IR-dyes - to induce absorption of light. Upon laser illumination the capsules containing light absorbing material were deformed or cut, thus providing the venue for remote release of encapsulated materials. This opens a range of opportunities for remote release of encapsulated materials in a variety of applications.

Internalisation of Capsules by Living Cells:

5 µm polyelectrolyte capsules made of PAH/PSS and labelled with quantum dots as fluorescent markers were administered to breast cancer cells in order to monitor adhesion of capsules to the cell surface, internalisation by cells and further tracking inside the cells. It was demonstrated that capsules were taken up by the cells and finally accumulated around the cell nuclei. Internalized capsules are mainly squeezed whereas those not taken up keep their original spherical shape **(Fig.3)**.

Similar behaviour was found for granulocytes and monocytes from human blood. FITC labelled capsules with last layer PAH, PSS or PGA were incubated with heparinized blood at 37°C for 30 min. Then the fluorescence of the leucocytes was studied by flow cytometry. The cell uptake was dependent on the surface charge and polymer composition.

Fig. 3: Image of polyelectrolyte capsules fluorescently labelled with quantum dots after internalisation by breast cancer cells (in collaboration with LMU München – Dr. W. Parak, Dr. A. Rogach)

Encapsulated Enzymes as In Vivo-Tools for Prodrug Activation:

Enzymes loaded into capsules have been shown to maintain up to 100 % of their original activity, as the encapsulation process stabilizes the native conformation of the enzyme and, moreover, inhibits degradation and dilution effects. In order to create a cell-residing microreactor capable of converting non-toxic precursors into toxic drugs, a bacterial alkaline phosphatase (AP) was assembled in the shell of 5 µm-sized hollow PAH/PSS-capsules by using an LbL approach. AP is known to convert doxorubicin phosphate into one of the most potent anticancer drugs, doxorubicin. AP immobilized in capsule-shells was shown to keep its enzymatic activity even after being internalized by breast cancer cells. Encapsulated enzymes like AP could be utilized as a novel, enzyme-mediated drug delivery system to fight various diseases.

G. Sukhorukov, A. Antipov, M. Bédard, A. Cordeiro, C. Déjugnat, R. Georgieva, D. Gorin, A. Günther, D. Halozan, K. Köhler, O. Kreft, T. Mauser, A. Petrov, A. Praast, M. Prevot, I. Radtchenko, S. Sadasivan, D. Shchukin, D. Shenoy, A. Skirtach, D. Volodkin,
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Key Publications:

[1] Köhler, K., Shchukin, D.G., Sukhorukov, G.B., Möhwald, H.: Drastic Morphological Modification of Polyelectrolyte Microcapsules induced by High Temperature. Macromolecules **37**, 9546-9550 (2004).

[2] Mauser, T., Déjugnat, C., Sukhorukov, G.B.: Reversible pH-dependent properties of multilayer microcapsules made of weak polyelectrolytes. Macromol. Rapid Commun. **25**, 1781-1785 (2004).

[3] Sukhorukov, G.B., Volodkin, D.V., Gunther, A.M., Petrov, A.I., Shenoy, D.B., Möhwald, H.: Porous calcium carbonate microparticles as templates for encapsulation of bioactive compounds. J. Materials Chemistry, **14** (14), 2073-2081 (2004).

[4] Shchukin, D.G., Sukhorukov, G.B.: Nanoparticle Synthesis in Engineered Organic Nanoscale Reactors. Adv. Mater. **16**, 671-682 (2004).

[5] Skirtach, A.G., Antipov, A.A., Shchukin D.G., Sukhorukov G.B.: Remote activation of capsules containing Ag nanoparticles and IR dye by laser light. Langmuir **20**, 6988-6992 (2004).

NON-PLANAR INTERFACES

Ordering of Functional Nanoparticles

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Aims

Nowadays the revolutionary confinement effects of electrons – associated with nanoparticles – and photons – associated with microparticles – evoke a robust impetus in studies of colloidal particles and their assemblies. Directing colloidal particle self-assembly may allow not only exquisite fabrication of complicated hierarchical structures on all length scales but also fine tuning of the interaction between particles, thus creating defined novel cooperative properties. Hence, the focus of our research activities is mainly laid on organization of colloidal particles of sizes spanning the nanometer to micrometer range. In order to engineer particle assemblies, we concentrate on establishment of strategies to selectively introduce new functionality on or in particles. As colloidal self-assemblies may provide excellent templates for particle organization, we are also concerned with construction of colloidal crystals with new and defined symmetry.

Results

A. Sub- or Microparticle Self-Assembly

Monodisperse colloidal spheres may self-assemble into 2D or 3D ordered structures with hexagonal or cubic packing symmetries, so called colloidal crystals. Due to their promising potential in the photonic crystal application, colloidal crystallization has been intensively explored by far. Nevertheless, colloidal crystals fabricated till now are rather simple in terms of their structural symmetry and function. Much of our research is dedicated to development of new crystallization methodologies and fabrication of new building blocks in order to diversify colloidal self-assembly structures and functionalities. Several examples are highlighted as follows:

(i) Binary Colloidal Crystals

We have established a simple and rapid way to alternately organize large and small spheres into ordered binary structures via a stepwise spin coating procedure. The resultant structures can be manipulated by the size ratio of small to large spheres and spin coating speed **(Fig. 1)**.

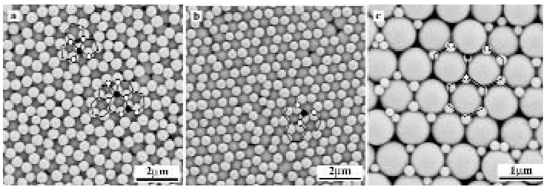

Fig. 1: SEM micrographs of the binary colloidal crystals produced by stepwise spin coating, in which small silica spheres were confined within the interstices between hexagonal close packed large ones.

As compared with the existing methods for binary colloidal crystallization, our method shows a large tolerance to the size ratio of differently-sized spheres and their size polydispersity. The possibility to extend our procedure into ternary colloidal crystals was demonstrated. Besides, this stepwise procedure may also create a capability to utilize the colloidal crystals for templating the organization of differently sized particles.

(ii) Nanocrystal-Tagged Hydrogel Spheres

Based on their stimuli-responsive swelling behavior, hydrogel spheres were tagged with CdTe nanocrystals with different sizes, realizing multiplex optical encoding **(Fig. 2)**, which should be of great importance for high throughput biological assays.

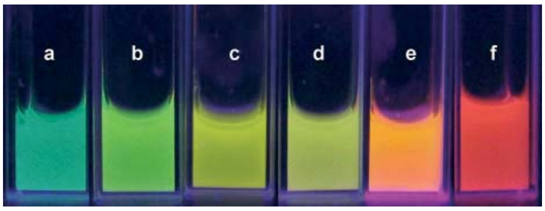

Fig. 2: Fluorescence images of hydrogel spheres incorporated with 2.5 nm (green) and 4 nm CdTe ones (red) and their mixtures with varied molar ratios.

Furthermore, the loaded nanocrystals may be released out of hydrogel spheres under a pH-trigger for example, which open up an opportunity for delivery of nanocrystals and their bioconjugates considering them as new drugs.

Using hydrogel spheres or those loaded with nanocrystals, we constructed solid non-close packed two dimensional colloidal crystals thanks to the large shrinkage of gel spheres after drying. The gap size of neighboring particles was altered with the concentration of the gel dispersions and withdrawing speed of the dip-coating process. In addition, the non-close packing arrays rendered the supporting substrates anti-reflective, efficiently reducing the reflection of light.

(iii) Patterning Microsphere Surfaces

Using the upper single or double layers of colloidal crystals as masks during Au vapor deposition, followed by peeling off these template layers, we created various Au patterns on the lower spheres **(Fig. 3)**.

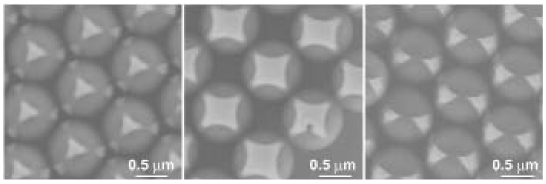

Fig. 3: SEM micrographs of polystyrene spheres with Au-patterned surfaces generated by templating the top monolayers of colloidal crystals with different crystal orientations.

The dimension and geometry of the Au patterns obtained are dependent on the orientation of the colloidal crystal templates. This patterning procedure is independent on the curvature and chemical composition of the surfaces, which definitely pave a promising way to pattern highly curved surfaces, especially of sub-or micron-sized objects.

B. Nanoparticle Self-Assembly

By coating the ligands bearing the terminal group of 2-bromopropionate, a specific surface wettability – the contact angle of close to 90 degree – was implemented on both hydrophobic and hydrophilic nanoparticles, which drive particles into water/oil interfaces and self-assemble into close packed arrays.The success of this interface attachment centers on the surface wettability of nanoparticles, predominantly depending the termini of the coating ligands. Based on this interface attachment, thin films consisting of different nanoparticles, for instance Au and Ag ones, were also constructed at the water/oil interface **(Fig. 4)**.

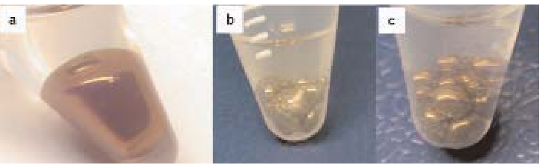

Fig. 4: Photographs of water droplets enclosed by thin films of Au (a) and Ag nanoparticles (a) and of their mixture, formed at the water/toluene interface.

Furthermore, the potential of stabilizing emulsion droplets based on the interfacial self-assembly of nanoparticles was demonstrated. The interface self-assembly may therefore pave an interesting and facile way to organize nanoparticles, generating two or three dimensional nanostructures for electronic, optic, and magnetic applications.

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Key Publications:

[1] Wang, D., Möhwald, H.: Template-directed colloidal self-assembly – the route to top-down nanochemical engineering. J. Mater. Chem. **14**, 459-468 (2004).

[2] Wang, D., Möhwald, H.: Rapid fabrication of binary colloidal crystals by stepwise spin-coating. Adv. Mater. **16**, 244-247 (2004).

[3] Duan, H, Wang, D., Kurth, D.G., Möhwald, H.: Directing self-assembly of nanoparticles at water/oil interfaces. Angew. Chem., Int. Ed. **43**, 5639-5642 (2004).

Molecular Assembly of Biomimetic Systems

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Aims

It is well known that most molecular recognition and signal transduction processes in biological systems occur at native cell surfaces, and the biological function of the receptors is regulated by soluble active substances. Both functional understanding of molecular recognition processes and their application in screening for effective compounds are very important in basic life science research and drug discovery. We constructed different types of biomimetic systems based on molecular recognition at membrane interfaces through molecular assembly as well as chemical reaction and intend to apply these for drug delivery, bimolecular separation and medical diagnosis.

Results

Biomolecular Recognition and Membrane Hydrolysis

The hydrolysis reaction of phospholipid monolayers at the air/water interfaces catalyzed by different enzymes, like PLA$_2$, PLD, PLC has been deeply studied by means of newly developed spectroscopic and microscopic techniques so that the mechanism of interfacial hydrolysis can be better understood. The morphological changes of lipid monolayers caused by the adsorption of enzymes, and the quantitative analysis of hydrolysis products are investigated. **(Fig. 1)**

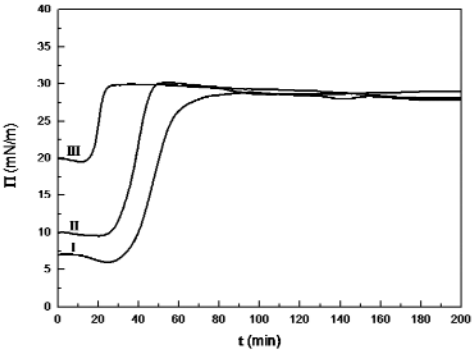
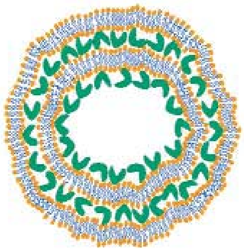


Fig. 1: Curves of surface pressure p as a function of time t of L-DPPC monolayer after the injection of PLC into the subphase at different initial pressures. C PLC = 10 units

A three-pronged investigative platform which combines novel hydrolysis experiments in reconstituted lipid membranes and cell biology with theoretical calculations as well as computer simulations has been formulated to meet our goals. We also tried to assemble F0F1-ATPase into biomimetic membranes in order to better understand the mechanism of biomolecular motors in biological environment.

Biogenic Microcapsules

On lipid bilayers assembled to the protein surface, the complex film serves as a biomimetic membrane. We fabricated multilayers of human serum albumin (HSA) and a phospholipid (DMPA) on the colloidal particle or drug crystal surface (Scheme I) through layer-by-layer assembly, followed by core removal to obtain HSA/DMPA hollow capsules **(Fig. 2a and 2b)**.



Scheme 1: Schematic illustration of HSA/DMPA multilayer assembly on the drug crystal surface

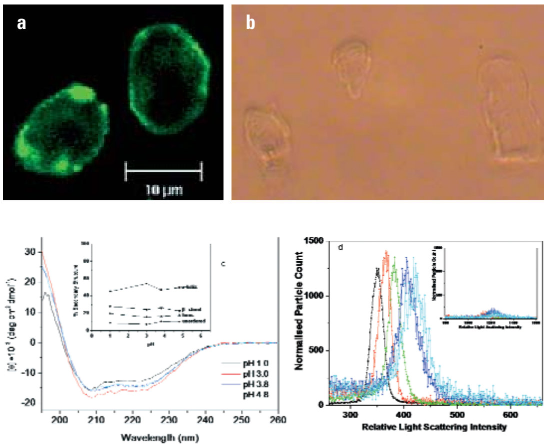


Fig. 2: (a) Fluorescence microscopic image of (HSA/DMPA)4 encapsulated ibuprofen crystals. 5% NBD-DMPC was used as fluorescent label. (b) Intact hollow capsules after the release of Ibuprofen crystals. (c) CD spectra of HSA at different pH values. (d) Single particle light scattering experiment confirms the bilayer structure of each lipid layer.

The detailed wall structures of the capsules were analyzed by various techniques **(Fig. 2c and 2d)**. It indicates that the well-defined lipid bilayer formed on the HSA surface will provide the possibility to incorporate membrane specific components like channels and receptors into the capsule's wall for specific recognition **(Fig. 2d)**. For controlled and sustained release it is important to reduce the permeability of capsules for small polar species, which in most cases enable small molecules to diffuse easily through the capsule walls. In order to imitate the barrier function of biological membranes, it was thus attempted to assemble lipids on the PE capsules to reduce the permeability for ions and small neutral molecules. The lipid may form bilayer structures and in some cases also multilayers on the capsule surface. In addition, biointerfacing of polyelectrolyte hollow capsules will allow one to control the lipid/polymer capsule in a predetermined size. The enzymatic reaction occurring at the surface alters the permeability of the capsule, which may lend the capsule new features. This procedure can be applied for biomimetic cells to study reactions in a living system.

Controlled-release drugs have many advantages over conventional dosage forms, such as minimizing deleterious side effects, prolonging the duration of activity, protecting sensitive drugs from enzymatic or acidic degradation, taste masking, and targeted release. Thus, controlled-release technologies are of interest to the pharmaceutical industry in the development of modern medications. We have chosen HSA and DMPA as a pair to fabricate multilayers by use of a recently developed layer-by-layer (LbL) self-assembly technique onto drug crystals and realized the encapsulation and controllable release of drugs **(Fig. 2b)**. HSA is a globular protein of known crystal structure and DMPA is an important lipid component of biological membranes. Complex films of proteins and lipids have unique biological properties, which makes them of significant interest as a model for biological membranes. With such a lipid/protein pair, the incorporation of membrane-specific components, such as receptor channels, into the films for the purpose of target release becomes feasible.

Fabrication of Nano Structured Biomaterials

For many biologically relevant systems, biogenic nanotubes are of specific significance. After successfully fabricating highly flexible nanotubes from water-soluble charged polymers by replication of pore templates, we developed the pressure-filter-template approach to assemble HSA and DMPA/HSA nanotubes with a monodisperse size distribution and uniform orientation with the alternate adsorption of HSA by varying the pH value at each deposition or mixed with DMPA **(Fig. 3)**.

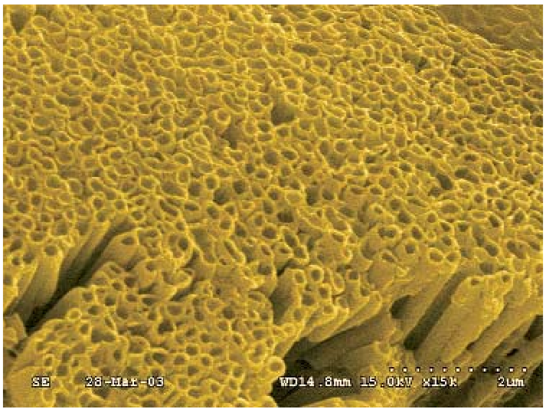


Fig. 3: Scanning electron micrographs of DMPA/HSA nanotubes obtained by template-based self-assembly

The modification of HSA structure or the lipid bilayer binding to HSA results in the high flexibility of both types of nanotubes. Under the experimental conditions presented here the CD spectra showed no dramatic change of the helix structure of HSA within a lower pH range. The nanotubes allow the specific incorporation of lipophilic components like channels or receptors and may thus serve as probes or sensors for biological systems.

Selective Control of Cell Adhesion on Patterned Substrates

Dynamic bindings and adhesive interactions between cells and their surrounding extracellular matrix (ECM) play central roles in nearly all aspects of the cell life, for example, in the regulation of many cellular processes including proliferation, differentiation, migration, and apoptosis etc. We have collaborated with Prof. Michael Grunze's group of Heidelberg University to use chemical lithography to control and monitor the compositional chemistry, mechanical properties, architecture and geometry of cell adhesive interactions **(Fig. 4a and 4b)**.

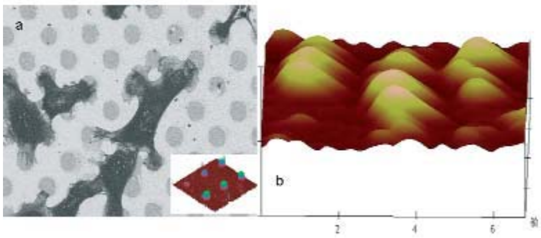


Fig. 4: Immobilizations of (a) RGD on patterned NIPAM polymer brushes and (b) liposomes on supported lipid bilayer patters.

By engineering well-defined cellular microenvironments, we could better understand the complex nature of the sensory and transduction systems for cell adhesion.

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Key Publications:

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RESEARCH GROUP NANOTECHNOLOGY FOR LIFE SCIENCE

A Cooperation between the MPI of Colloids and Interfaces and the Fraunhofer Institute of Applied Polymer Research

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The research group nanotechnology for life science started in April 2002 and is a joint research program between the Fraunhofer Institute for Applied Polymer Research and the Max Planck Institute of Colloids and Interfaces. Our research mainly focuses on potential applications of macromolecules in all aspects of human medicine (delivery, diagnostics, biomaterials). Thus, our main philosophy is to create a bridge between innovative fundamental polymer/material science and Life science industry. Our research program can be decomposed into three main aspects **(Fig. 1)**.

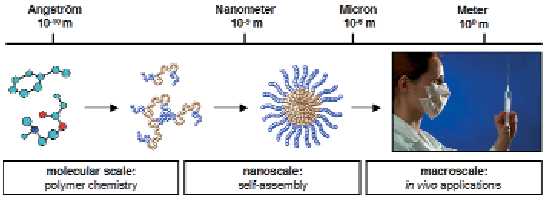

Fig. 1: Strategy for preparing tailored nanostructures for life-science applications

1. At the Molecular Scale: Designing New Macromolecules for Life Science.

Our first objective is to prepare at the molecular level well-defined macromolecules with a life science potential, such as water soluble polymers, amphiphilic copolymers, hybrids of synthetic polymers and biomacromolecules, biodegradable polymers, polymer bioconjugates, stimuli responsive polymers… For reaching this goal, we are using and combining several modern methods of synthesis such as controlled radical polymerization **[1,2]**, living polymerization of polypeptides **[3]**, ring opening polymerization or click chemistry **[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). A good example of our synthetic work is the preparation via radical polymerization of synthetic polymers and copolymers bearing nucleic acids moieties such as thymine, adenine or uracil **[5]**. These original polymers were prepared using controlled radical polymerization techniques and possess a good potential for interacting with natural biomacromolecules such as DNA or proteins and therefore can be used in bioseparation devices. The properties of such macromolecules are currently under investigation in a cooperation project with Andreas Thünemann at the Bundesanstalt für Materialforschung und -prüfung (BAM, Berlin).

2. At the Nanoscale: Preparing Nanostructures via Self-assembly of Polymer Building Blocks.

Well-defined polymers (as described in the previous paragraph) are our main building blocks for preparing nanostructures. Various types of nanostructures were prepared from segmented copolymers (i.e. block or graft copolymers) in our laboratory during the last few years **(Fig. 2)** such as nanoaggregates capable to transport DNA into living cells (polyplexes), stealth-nanoparticles, which can be used in several aspects of nanobiotechnology or micellar assemblies (micelles, vesicles), which possess an enormous applicative potential as nanocontainers for drug delivery.

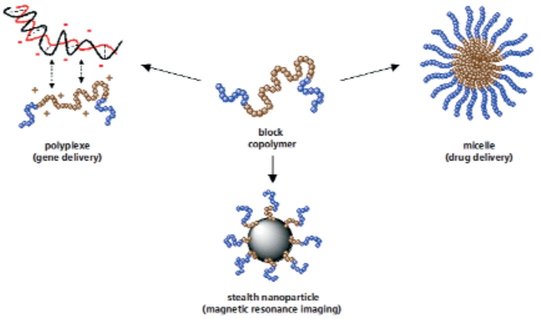

Fig. 2: Various nanostructures obtainable via the self-asembly of segmented copolymers

In all cases, our goal is to develop innovative polymer-based nanostructures with a high applicative potential in medicine. A good example of this philosophy is our recent work concerning the preparation and characterization of multicompartment micelles **[6]**. The latter is a collaboration with Professor Möhwald (MPI, Interfaces department). Multicompartment micelles composed of a water-soluble shell and a segregated hydrophobic core are very interesting structures for nanobiotechnology, since the separated incompatible compartments of the hydrophobic core could enable the selective entrapment and release of various hydrophobic drugs while the hydrophilic shell would permit to stabilize these nanostructures in physiological media. Very recently, we successfully built multicompartment micelles from the direct aqueous self-assembly of amphiphilic ABC triblock copolymers possessing a gradient of hydrophobicity: one hydrophilic segment and two incompatible hydrophobic segments (one hydrocarbon segment and one fluorocarbon segment) **[7]**. The nano-segregated morphology of these unusual objects was studied and characterized using several analytical techniques such as dynamic light scattering, ultra-centrifugation, small angle X-ray scattering or cryo-TEM.

3. At the Nano- or Macroscale: Evaluating the Applicative Potential of Polymer Nanostructures In Vitro or In Vivo.

This last point of our research program is not directly developed in our laboratory. Our research skills are principally the synthesis of polymers and self-assembly of polymers into nanostructures (paragraphs 1 and 2). Therefore, all the *in vitro* or *in vivo* tests of our nanostructures are done via external collaborations. For example, we built during the last few years a productive collaboration with the group of Dr. Rudolph at the Ludwig Maximilians University (LMU) of Munich on non-viral gene delivery. The group of Dr. Rudolph studies *in vivo* and *in vitro* the transfection capabilities and the toxicity of new DNA carriers prepared in our laboratory. Another example of fruitful association is our collaboration with the research group of Professor Pison (department of radiology, Charité, Berlin). In this project, we are testing nanoparticles composed of a magnetic inorganic core and a polymer shell as new contrast agents for magnetic resonance imaging. Our first goal during the last three years was to study the *in vivo* behavior of such colloids and it was evidenced that our polymer coating prevents significantly the capture *in vivo* of the nanoparticles by the immune system. Our nanoparticles were circulating around 24 hours in the rat bloodstream before being captured by the liver cells. Classically magnetic nanoparticles, which do not possess polymer coating are captured in less than 5 minutes by the liver cells. Such a result is a tremendous improvement, which opens wide applicative possibilities. Another very important subject of research in our laboratory is Alzheimer disease. For instance, we investigate the aggregation of amyloid peptides on various model surfaces (flat surfaces or colloidal systems) **[8]**. The target of this project is to find specific surface coatings, which efficiently prevent the formation of the amyloid plaques. The model surfaces are modified with various polymer coatings prepared in our laboratory and are studied in the group of G. Brezezinski.

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