INTERFACES

Research in the Department of Interfaces

I. General Strategy

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

As a general trend in all groups the interfaces increase in complexity, i.e. planar interfaces mostly also contain proteins, polypeptides or nanoparticles. If the interface contains only small molecules the dynamics is of prime importance. A sole exception of the above are studies concerning the old and new problem of water structure at the interface and the arrangement of peculiar groups like CF_2 at interfaces.

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

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

II. Research Highlights
II. 1 Planar Interfaces

Insoluble monolayers at the air/ water interface as most suitable model system are made use of in the group of *G. Brezesinski* studying polypeptides, phospholipids, DNA binding and enzymatic hydrolysis and phosphorylation at interfaces, the leading techniques being FTIR-spectroscopy and X-Ray scattering. X-Ray fluorescence is introduced to measure the specific ion binding to monolayer surfaces and, surprisingly, monovalent ions like Cs^+ may effectively replace divalent ones (Ca^{2+}). For an antibiotic peptide it is demonstrated how it binds to the membrane to destabilize it. New cationic lipids with high transfection potential are shown to align
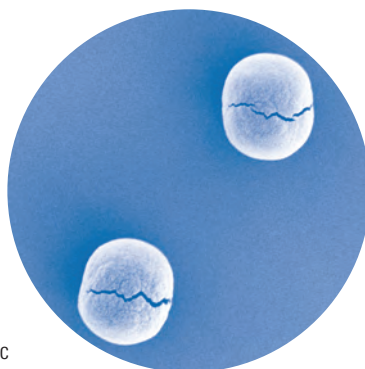
DNA coupling to an interface. The binding of the enzyme phospoinositide-3-kinase is shown to depend on lipid phase and charge and also its products are miscible in the membrane to a different extent.

The group of *H. Motschmann* has shown by IR-Vis sum frequency spectroscopy that large and polarisable ions adsorb to a water surface in an oriented way and also distort the water structure. Vibrational modes of even highly symmetric molecules are measured, apparently due to the symmetry break encountered at the interface.

The group of *R. Miller* has demonstrated that protein/ surfactant complexes may have different surface activity depending on their stoichiometry. They may be more hydrophobic and replace surfactant at the interface or they may become more hydrophilic and thus be soluble in water. This could be demonstrated by dynamic surface tension studies as well as by shear rheology.

The group of *R. Krastev* has qualitatively explained the unusual drainage velocity of foam films and found a bridging effect for rod-like ions. They managed to prepare asymmetric films of polyelectrolytes suitable for vectorial charge transfer and could arrange layers of magnetic nanoparticles. These, due to aggregation showed response measured by spin-polarized Neutron reflectivity.

The group of *H. Riegler* has shown for C60 droplets that line tension may affect the shape of adsorbed aggregates. For alkanes as model adsorbates with exclusively van-der-Waals interactions, the melting point reduction at a surface could be converted into interaction potentials. It was shown to quantitatively differ comparing alkanes with fatty acids. This group is now also extending their studies on controlled nucleation and growth at surfaces towards nanostructured films that may become relevant for organic photovoltaics.

II. 2 Non-Planar Interfaces

The complexation of bisterpyridines and metal ions studied in the group of *D. Kurth* was shown to be highly dynamic. Combining analytical ultracentrifugation (coop. with *H. Cölfen*, Coll. Chem.) and simulations of rate equations (coop. with *T. Gruhn*, Theory) the unusual dependence can be explained almost quantitatively. The polymer length was also found to differ in solution and at interfaces which can be qualitatively understood (coop. with *J. Raabe*, Humboldt Univ.)

The group of *D. Shchukin* has been extremely successful in developing coatings with feedback activity. This was made use of in anticorrosion coatings and is also promising for antifungal coatings and containers delivering energy on demand. The ideas and experiments have become most fruitful that the group attracted much funding, including direct industry funding.

Major activity of the group of *D. Wang* concerned the funcionalization of nanoparticles to switch their surface activity. Meanwhile they could show the reversible phase

transfer of metallic and magnetic nanoparticles. Also their aggregation could be reversibly changed via temperature and salt enabling switching on and off collective optical and magnetic properties.

It was shown in the former groups of *A. Fery* and *G. Sukhorukov* that glass transitions can be induced in polyelectrolyte multilayers via salt and temperature (20-50°C), and in the high temperature state the film is permeable for large and small molecules. Incorporating metallic nanoparticles into these films tremendously increases IR absorption, due to the low heat conductivity of the surroundings temperatures may by locally increased by up to 100°C, and this hot spot can be confined to some 10 nm. This is quantified by simulations and experiments in the group of *A. Skirtach* using this for remote and controlled release of drugs inside cells and for hot nanoembossing.

In the International joint laboratory with the Chinese Academy of Science led by *Junbai Li* heating of capsules followed by cooling is used to anneal defects such that they become impermeable to small drugs at room temperature. These capsules have been equipped with specific recognition sites to enable transport by molecular motors. Here capsules are good "model cargos" to understand the mechanisms because size and surface can be manipulated in a defined way.

T. Nakanishi has taken over the leadership of the joint laboratory with the "National Institute for Materials Science" in Tsukuba. He used fullerenes with attached aliphatic tails as building blocks to obtain hierarchical structures with lamellae and micelles as basic units. He thus could obtain stable ultrahydrophobic coatings and films with high (two-dimensional) charge carrier mobility. In addition the flower-like structures could be templated to obtain metal surfaces with high specific area suitable for electrochemical and Raman studies.

The results of the joint laboratory (Laboratoire Européen Assciee (LEA) with the institute of separation chemistry (ICSM) in Marcoule on sonochemistry, active since 01.01.2008 on sonochemistry are listed in *D. Shchukin's* report who also leads this laboratory. The success, preparing new nanostructures with specific catalytic, optical and encapsulation properties by this highly nonequilibrium process is documented in many publications. Lacking is the mechanistic understanding for which optical experiments of single and multi-bubble luminescence are now set up.

III. Future Development

Major changes of staff in the last 2 years have been:
· *R. Krastev* has moved as a group leader to the institute of natural and medical science at the Univ. Tübingen. His work on foam films will be terminated with a student and a post-doc finishing this year. The work on multilayer films will be continued in collaboration with the aim of establishing bioresponsive and magnetoresponsive films.
· *H. Motschmann* accepted the offer of a professor position at Univ. Regensburg. His group has moved there taking with them the equipment for nonlinear optical spectroscopy.

· *D. Kurth* has moved as professor to Univ. Würzburg. The activities of his group will be terminating with the last two graduate students finishing.
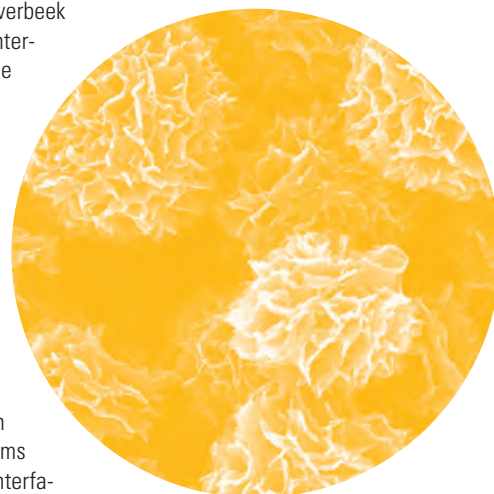
Since I intend to retire in 2011 plans for the future are dominated by the need to develop a career of scientists, not having permanent positions in the institute, at some attractive places outside. This basically means strengthening cooperations and attracting funding that people could work in outside laboratories. Thus responsive multilayer films will be pushed within the Campus project on "Bioactive Surfaces", and hydrogels are central in a collaboration with TU Berlin within the Excellence Center on Catalysis. Responsive nanoparticles are in the focus of collaborations with medicine (Charité), biochemistry (Univ. Münster) and pharmacy (Univ. Saarbrücken). Self-repairing coatings have already developed very well in collaborations and funding and will provide many opportunities for the scientists involved. I expect this also for the started activities on sonochemistry where we would like to introduce more surface science and understanding and later transfer knowledge and scientists to France.

With these collaborations mentioned above the funding and the scientific output could be maintained at a high level as well as the size of about 80 persons. It will have to be reduced by a factor of 2 within the next 2 years, and so the main challenge will be to help the many highly motivated co-workers find attractive positions.

Major awards have been given to *T. Nakanishi* and to me in person. I received the Overbeek medal of the European Colloid and Interface Society in 2007, will obtain the Wolfgang-Ostwald award of the Kolloid-Gesellschaft in 2009, the most senior awards of both societies, and in 2008 a honorary doctorate of Univ. Montpellier 2.

My colleagues are continuing their efforts to continue having a department of interfaces with a new director following me. The success, however, is still uncertain. Obviously I would also be very disappointed if they would not succeed in view of the many interesting problems and the fundamental importance of interfacial science for understanding and controlling any hierarchical structure. On the other hand our activities were not confined to one institute and one country and therefore it is the recognition world-wide which counts and which persists beyond our scientific life time. There have been many co-workers in the department working with pleasure and developing their career in many countries, and therefore the knowledge is not only on paper but also in heads, the most important know-how transfer.

Helmuth Möhwald
Director of the Department of Interfaces

Langmuir Monolayers as Model Systems to Study Interactions at Interfaces

Gerald Brezesinski 02.04.1950

1974: Diploma, Biophysics (Lomonossow University of Moscow)
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 (Max Planck Institute of Colloids and Interfaces, Potsdam)

References:

[1] Shapovalov, V. L., Ryskin, M. E., Konovalov, O. V., Hermelink, A. and Brezesinski, G.: Elemental analysis within the electrical double layer using total reflection X-ray fluorescence technique. J. Phys. Chem. B **111**, 3927-3934 (2007).

[2] Koelsch, P., Viswanath, P., Motschmann, H., Shapovalov, V. L., Brezesinski, G., Möhwald, H., Horinek, D., Netz, R. R., Giewekemeyer, K., Salditt, T., Schollmeier, H., von Klitzing, R., Daillant, J. and Guenoun, P.: Specific ion effects in physicochemical and bioQi, W., Li, D.X., Wang, K.W., Yan, K.W., Cui, Y., He, Q., Li, J.B., ATP synthesis catalyzed by motor protein CF0F1

Determining structure/function relations for proteins/peptides and lipids requires a milieu that mimics the interfacial environment in which the molecules function. Monomolecular films at the air/water interface are membrane model systems which can be easily varied in terms of lipid composition, lipid lateral packing density, surface pressure and area exposed to the medium. The interactions of dissolved biomolecules with the membrane model interface can change the lipid packing density. On the other hand, lipid structural properties can dictate the adsorption behavior of proteins/peptides. During the last years we have concentrated our efforts on ions **[1, 2]**, DNA **[3, 4]**, enzymes **[5-8]** and peptides **[9-11]** at interfaces.

Ion Specific Effects

The total reflection x-ray fluorescence (TRXF) technique has been developed to be a truly simple tool for elemental analysis within the electrical double layer (EDL) near charged monolayers at the air/water interface (cooperation with Dr. V.L. Shapovalov, IPC RAS Moscow, Russia). The vast majority of counterions is concentrated in the thin inner part of the EDL irrespective of the electrolyte concentration in bulk. Using highly charged monolayers, univalent Cs^+ is quite competitive with divalent Ca^{2+} and Ba^{2+} in the formation of the EDL (which contradicts the classical Gouy-Chapman model). If the univalent/divalent ion ratio in bulk is 9:1, the corresponding ratio in the EDL is ca. 1.5 for Cs^+/Ca^{2+} and 0.5 for Cs^+/Ba^{2+}, whereas the model predicts 0.14 only. Bearing in mind packing density limitations, these values are consistent with a series of sizes for hydrated ions: $Cs^+ \ll Ba^{2+} < Ca^{2+}$ **[1, 2]**.

TRXF was also used to determine the protonation rate of new compounds designed for versatile DNA delivery systems. The head groups of these cationic lipids, represented by monoamines or oligoamines, can be charged or uncharged in dependence on the environmental pH. Since their pK values are unknown, the 2D concentration of bromide counterions was estimated by comparing the fluorescence intensity with that of DODAB monolayers as a reference **(Fig. 1)**.
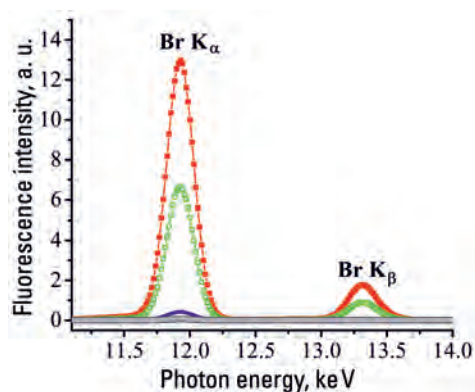
The monolayers of all studied compounds are completely uncharged at pH values above 10. The influence of the monolayer packing density on the protonation properties is clearly shown **[3]**.

Lipids for Gene Transfection

In order to obtain more effective and safer liposome-based gene transfection systems, new cationic lipids have been synthesized in the group of Prof. B. Dobner (University of Halle). The new lipids were studied in 2D as well as in 3D systems. The results show clear differences in structure and phase behaviour in dependence on the subphase pH due to protonation or deprotonation of the lipid head group. The packing properties of the molecules in mono- and bilayer systems are very similar. DNA couples to the lipid monolayers at low as well as at high pH, but in different amount. The DNA coupling leads to an alignment of adsorbed DNA strands **(Fig. 2)**. The distance between aligned DNA strands does not change much if the lipid layer is condensed **[4]**.
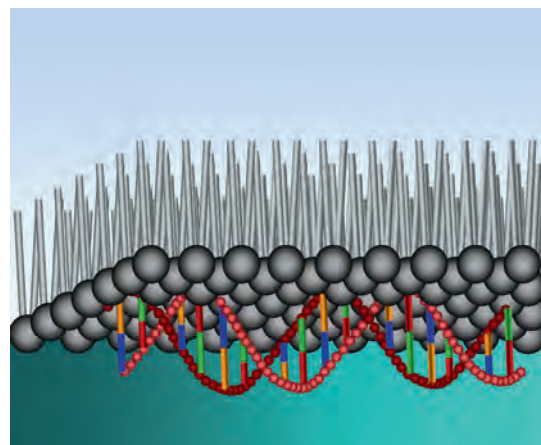
Fig. 2: Molecular model of DNA ordering at the monolayer of the novel cationic lipids.

Fig. 1: Selected X-ray fluorescence spectra of the lipid monolayer at 40 $Å^2$·molecule^{-1} on Br$^-$ containing subphases at pH 3 (■), pH 6 (□), pH 8 (●) and pH 11 (○).

Phosphoinositides and Phosphoinositide 3-kinase γ

Phosphatidylinositol and its phosphorylated derivatives play crucial roles in a broad range of signal transduction processes. To shed light on processes that lead to the formation of phosphoinositide-enriched microdomains, mixed monolayers were investigated [7]. DOPtdIns is capable to mix partially with condensed DSPC and to form mixed crystals which differ significantly from those formed by pure DSPC. DOPtdIns(4,5)P_2 in mixtures with DSPC is to a much larger extent phase separated (Fig. 3). In biological systems, an enzymatic phosphorylation of phosphatidylinositol in mixed domains may cause their insolubility in ordered PC areas and leads to a cooperative reorganization of the host lipid membrane.
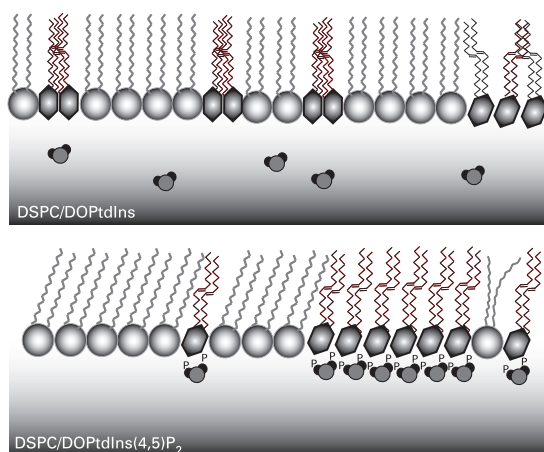

Fig. 3: Scheme of the molecular arrangement in the investigated mixtures. The non-phosphorylated inosites (DOPtdIns) are partly distributed within the condensed DSPC layer (top) and are able to change the orientation of the DSPC molecules. Oppositely, the highly charged DOPtdIns(4,5)P_2 is mostly phase separated (bottom). The water molecules interact with the DOPtdIns(4,5)P_2 and stabilize this phase.

The recruitment of phosphoinositide 3-kinase γ (PI3Kγ) to the membrane is the crucial requirement for the initiation of, e.g., inflammation cascades by second messenger production (cooperation with Prof. R. Klinger, University of Jena). The adsorption behavior of GST-PI3Kγ to non-substrate as well as substrate lipids was investigated by Infrared Reflection Absorption Spectroscopy (IRRAS). The enzyme does not interact with condensed zwitterionic or anionic monolayers. However, it can penetrate into uncompressed fluid monolayers. Protein affinity for the monolayer surface is considerably increased when the lipid has an anionic head group and contains an arachidonoyl fatty acyl chain in sn-2 position [8]. The protein adsorption has a condensing effect in phosphoinositide monolayers.

Antimicrobial Peptides

Over recent decades a broad spectrum of antimicrobial peptides (AP) has been identified as a native line of defense in animals, plants, and also in single-cell organisms. They are also of great scientific interest because they are promising candidates for the development of novel therapeutics. We have studied the interactions of APs with different surfaces using a large variety of modern methods (cooperation with Dr. J. Andrä, Research Center Borstel). NK-2 is an antimicrobial peptide derived from the cationic core region of porcine NK-lysin. It adopts an unordered structure in water, buffer, and in the presence of monomeric cationic and non-charged amphiphiles. However, it forms a stable α-helix in 2,2,2-trifluoroethanol (TFE) and in micellar solutions of anionic, cationic as well as nonionic amphiphiles. NK-2 is surface active and forms a Gibbs monolayer at the air/buffer interface. In contrast, no adsorption was observed if NK-2 is dissolved in water. During the adsorption process in buffer solutions, NK-2 undergoes a conformational transition to an α-helix which lies flat at the interface. This is confirmed by X-ray reflectivity (XR) measurements (Fig. 4) revealing that the adsorption layer of the peptide NK-2 possesses a thickness of 17 Å [10].
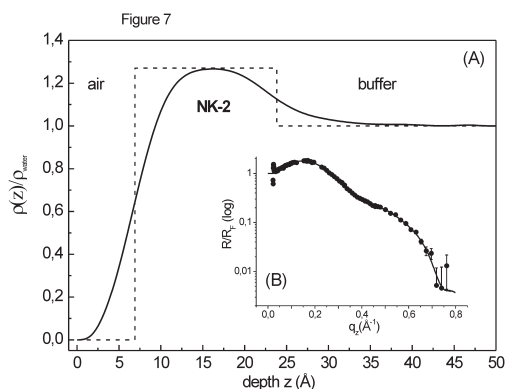

Fig. 4: Specular X-ray reflectivity normalized by the Fresnel reflectivity, $R(q_z)/R_f(q_z)$ (inset B) and the corresponding electron density profile (solid line in A) of NK-2 adsorbed at the air/buffer interface. The dashed lines represent the one-box model used to describe the electron density profile. Solid line in panel B is the best fit using a model-independent approach.

The peptide film is very stiff and can be compressed if trapped at the water surface. In contrast, the secondary structure (α-helix) of the AP dicynthaurin is maintained upon adsorption. XR and IRRAS showed the destabilization of the condensed phase of a pure DPPG monolayer. Penetration of the peptide was found to be pressure dependent. The results suggest that the APs are able to adsorb to PG-rich cytoplasmic membranes of bacteria and alter membrane integrity [11].

G. Brezesinski, M. Antipina, A. Hermelink, M. Hörnke, A. Muenter, C. Olak, G. Reiter, A. Saraiva, E. Soussan, O. Travkova, C. Stefaniu, K. Wagner
gerald.brezesinski@mpikg.mpg.de

reconstituted in lipid-coated hemoglobin microcapsules. Adv. Mater. **20**, 601-605 (2008).

[3] Antipina, M. N., Dobner, B., Konovalov, O. V., Shapovalov, V. L. and Brezesinski, G.: Investigation of the protonation state of novel cationic lipids designed for gene transfection. J. Phys. Chem. B **111** ,13845- 13850 (2007).

[4] Antipina, M. N., Schulze, I., Dobner, B., Langner, A. and Brezesinski, G.: Physicochemical investigation of a Lipid with a new core structure for gentrans-fection: 2-Amino-3-hexadecyloxy-2-(hexadecyloxymethyl)propan-1-ol. Langmuir **23**, 3919-3926 (2007).

[5] Wagner, K. and Brezesinski, G.: Phospholipase D activity is regulated by product segregation and the structure formation of phosphatidic acid within model membranes. Biophys. J. **93**, 2373-2383 (2007).

[6] Wagner, K. and Brezesinski, G.: Phospholipases to recognize model membrane structures on a molecular length scale. Curr. Opin. Colloid Interface Sci. **13**, 4-53 (2008).

[7] Hermelink, A. and Brezesinski, G.: Do unsaturated phosphoinositides mix with ordered phosphadidylcholine model membranes? J. Lipid Res. **49**, 1918 -1925 (2008).

[8] Hermelink, A., Kirsch, C., Klinger, R., Reiter, G. and Brezesinski, G.: Adsorption of GST-PI3Kγ at the Air/Buffer Interface and at Substrate and Non-Substrate Phospholipid Monolayers. Biophys. J. in press (2009).

[9] A.H. Muenter, J. Hentschel, J., Börner, H.G. and Brezesinski, G.: Characterization of peptide-guided polymer assembly at the air/water interface. Langmuir **24**, 3306-3316 (2008).

[10] Olak, C., Muenter, A., Andrä, J. and Brezesinski, G.: Interfacial properties and structural analysis of the antimicrobial peptide NK-2. J. Pept. Sci. **14**, 510-517 (2008).

[11] Bringezu, F., Majerowicz, M., Maltseva, E., Wen, S., Brezesinski, G. and Waring, A. J.: Penetration of the Antimicrobial Peptide Dicynthaurin into Phospholipid Monolayers at the Liquid-Air Interface. ChemBioChem **8**, 1038-1047 (2007).

Thin Soft Films

Rumen Krastev 24.01.1960
1985: Diploma, Chemistry
(University of Sofia, Bulgaria)
Thesis: Permeability of Gases
in Foam Films
1995: PhD, Physical Chemistry of Inter-
faces (University of Sofia, Bulgaria)
Thesis: Gas Permeability of
Black Foam Films
1986: Lecturer in Colloids and Interfa-
ces (University of Sofia, Bulgaria)
1993: Research Specialisation
(University of Bristol, UK)
1996-1997: Postdoc
(Max Planck Institute of Colloids
and Interfaces, Potsdam)
2002: Research Scientist
(Hahn Meitner Institute, Berlin)
2005-2008: Group Leader
(Max Planck Institute of Colloids
and Interfaces, Potsdam)
Since 2008: Group Leader,
Biomaterials (NMI Naturwissen-
schaftliches und Medizinisches
Institut an der Universität Tübingen,
Reutlingen).

References:

[1] P. Claesson, C. Stubenrauch,
R. Krustev, I. Johansson
Thin Film and Foam Properties of
Sugar-Based Surfactants; in Sugar-
Based Surfactants: Fundamentals and
Applications (Cristobal Carnero Ruiz ed.)
(2008), Taylor&Francis, LLC
[2] R. Farajzadeh, R. Krastev and P .L. J.
Zitha Foam film permeability:
Theory and Experiment Adv. Coll. Inter.
Sci. **137**, 27, (2008).
[3] R. Farajzadeh, R. Krastev and P. L. J.
Zitha Foam Films Stabilized with Alpha
Olefin Sulfonate (AOS)
Coll. and Surf. A: **324**, 35, (2008).

We study the properties of matter when it is organised in thin layers. These are layers with a thickness not more than 100 nm. Interactions between the surfaces are active in such systems and govern their properties to large extent. Such thin layers can be used to perform model studies on the interactions in the colloidal systems or to study the organisation of different species in two dimensions (2D). We use two systems for our studies – thin free standing (foam) films and polymer (polyelectrolyte) films on solid support.

Foam films

Foam films fascinate with their wonderful play of colours, but they also have been used for long time to study the strength of interactions between fluid (gas/liquid or liquid/liquid) interfaces. Such films can have a thickness of only few nano meters, but areas up to few square meters. This makes them easy for preparation with well reproducible molecular flat surfaces. The foam films consist of an aqueous core sandwiched between two adsorbed surfactant layers. The films are generally prepared from a drop of an aqueous surfactant solution. Under the action of capillary pressure and attractive interaction forces between the film surfaces, the liquid is expelled from the drop and a film is created. The film thickness, h, decreases until the equilibrium is reached. First common black films (CBF) are formed during the thinning process. When the electrolyte concentration in the film forming solution is properly chosen, thinner Newton black films (NBF) are formed in the CBF. The transition from CBF to NBF is a stochastic process and its probability depends on the strength of double layer electrostatic repulsion between the film surfaces.

Effect of the Shape of the Ions on the Electrostatic Interactions
(together with K. Bohinc, Lublijana)
The forces operative between the film interfaces according to the classical DLVO theory are expressed as disjoining pressure (Π) in the case of thin films. Π has an attractive van der Waals component Π_{VW} and a repulsive double layer electrostatic component Π_{EL}. The strength of Π_{EL} decreases strongly when ions are added to the aqueous phase of the film. This makes the films thinner and in extreme case they can rupture. Π_{EL} depends also strongly on the charge of the added ions. We focused our attention on the influence of the shape of the ions on Π_{EL}. We measured the thickness of films prepared from the non-ionic surfactant Dodecyl Maltoside (C12G2) in presence of spermidine and compared the results to those obtained in presence of NaCl. Spermidine is a three valent rod-like ion. The films prepared in presence of spermidine have the same equilibrium thickness as that of the films in presence of NaCl. There is no difference in the velocity of film thinning also. The major difference is that the probability of formation of NBF in the thicker CBF is much faster in the case of films prepared with spermidine **(Fig. 1)**. The results

show that the presence of rod-like ions in the solution facilitates the transition of CBF to NBF most probably by "bridging" the opposite film surfaces.
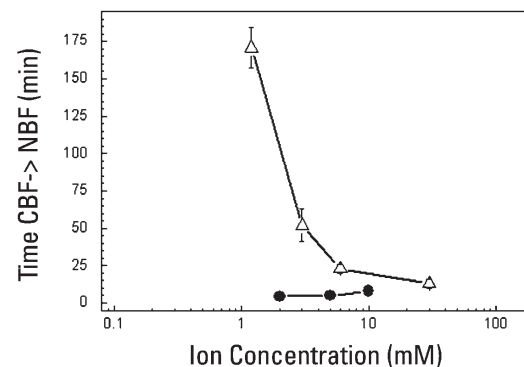

Fig. 1: Time for formation of NBF in the thicker CBF as a function of the ion concentration. Δ - in presence of 0.2 M NaCl; ● - in presence of spermidine with equivalent number of charges.

Foam Films from Ionic Liquids
Ionic liquids (IL) are liquids with the nature of salts. They are composed of cations and anions only. Besides non-volatile, ILs are non-flammable, thermally stable and structurally tuneable. All of these advantages make them a promising replacement for the traditional volatile organic solvents. We proved if stable foam films can be prepared from pure ionic liquid. Studying the interactions between the surfaces of the films made from IL we aim to shed more light on their structure near interfaces. We studied films formed with the IL [EMIM]$^+$BF$_4^-$. Formation of stable foam films only from IL was not possible. Addition of surfactant (e.g. 0.1 mM Brij35) was necessary to stabilise the films. Further studies are necessary to conclude if the ordering of the IL near interfaces as already reported may stabilise the films.

GISAXS from Foam Films
(cooperation P. Müller-Buschbaum, München)
Many experiments with foam films study the organisation of matter normal to the film surface. GISAXS allows to study the in-plane structure of the films and to probe organisation of nano defects (e.g. distribution of nano particles) in it. We performed first GISAXS experiments with foam films prepared from solutions of C12G2 and NaCl. Nano sized metal particles with a diameter of ca. 12 nm were added to the film forming solution. The scattering image of the 2D position sensitive detector at the beam line BW4 at DESY Hamburg is shown in **Fig. 2**. Well pronounced satellite reflections are visible which confirms formation of ordered structures in the plane of the film. This result opens possibilities to use foam films to organise small particles in well ordered structures.
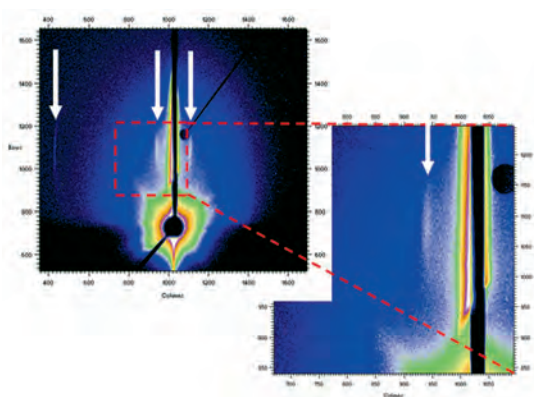
Fig. 2: GISAXS images from foam films which contain metal particles with a diameter of ca. 12nm.

Polyelectrolyte Films on Solid Support

We aimed to understand the organisation of polyelectrolytes (PE) in multilayers (PEM) and thus to be able to use them to build complex materials. We studied the effect of the first PE layer which assures the contact between the film and the support, the effect of the film post treatment and the film preparation (dipping vs. spraying) on the film thickness and density. We found that the ordering of nanoparticles on/in PEM depends on the treatment of the films. The NP were uniformly distributed in freshly prepared samples while only a highly concentrated layer of NP was formed when the PEM were exposed to elevated temperature after their preparation. The observed effect was correlated to glass-melt transitions of the PEM. We have studied magnetic response of magnetite-PEM composites. We found magnetic response which proved formation of the nano composites with appropriate high concentration of magnetic nanoparticles **(Fig. 3)**.
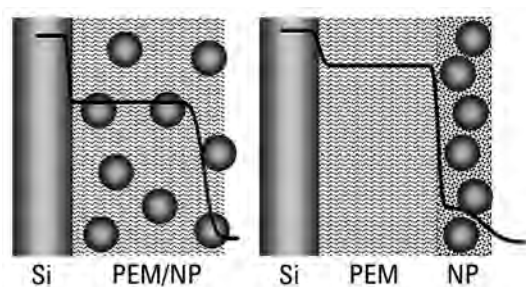

Fig. 3: Formation of composite films of PEM and magnetite nanoparticles. Left – fresh prepared samples; right – after temperature treatment. The lines present the change in the neutron scattering length density in the samples. .

Formation of asymmetric lipid layers was successful applying only one single lipid bilayer from the phospholipid DMPE and using its sensitivity to the pH of the solution. The bilayer was formed on PEM prepared with two strong polyelectrolytes - PSS and PDADMAC. The DMPE was always deposited onto the PEM cushion terminated with positively charged PDADMAC. The surface charge of the DMPE-coated film depends on the pH of the buffer solution. Formation of PEM could be continued on the top of the lipid bilayer by tuning the head group charge of the DMPE. An asymmetric structure of the PEM/DMPE/PEM "sandwich" was created in the case where anionic PSS was used as the first layer of the subsequent PEM. In this system, the DMPE lipid membrane was constructed as a charge asymmetric barrier sandwiched in the interior of the PEM films.
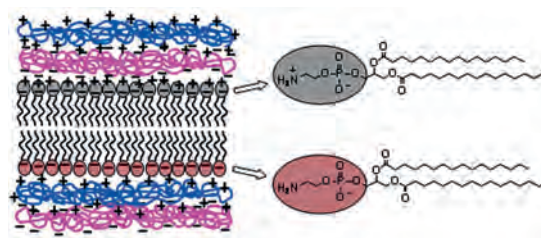

Fig. 4: A schematic structure of the PE multilayer architecture of sandwiched asymmetric lipid bilayers.

R. Krastev, J. Blacklock, P. Blecua, J. Chen, J. Früh, M. Kolasinska, R. Köhler, H.-J. Müller (emeritus). S. Stöckle, D. Volodkin, L. Xin, R. Emrich
rumen.krastev@mpikg.mpg.de
rumen.krastev@nmi.de

[4] R. Farajzadeh, R. Krastev, and P. L. J. Zitha Gas Permeability of Foam Films Stabilized by an α-Olefin Sulfonate Surfactant. Langmuir, **25**, 2881 (2009).
[5] M. Kolasinska, R. Krastev, P. Warszynski: Characteristics of polyelectrolyte multilayers: Effect of PEI anchoring layer and post treatment after deposition. J. Coll. Inter. Sci. **305**, 46, (2007).
[6] M. Kolasinska, R. Krastev, T. Gutberlet, P. Warszynski: Swelling and Water Uptake of PAH/PSS Polyelectrolyte Multilayers Progress in Colloid and Polymer. Science **134**, 30, (2008).
[7] M. Kolasinska, R. Krastev, T. Gutberlet, P. Warszynski: Layer by layer deposition of polyelectrolytes. Dipping vs. Spraying Langmuir **25**, 1224, (2009).
[8] J. Chen, R. Köhler, T. Gutberlet, H. Möhwald, and R. Krastev: Assymetric Lipid Bilayer Sandwiched in Polyelectrolyte Multilayer Films through Layer-by-Layer Assembly Soft Matter **5**, 228, (2009).
[9] N. Krasteva, H. Möhwald, R. Krastev: Structural changes in stimuli-responsive nanoparticle/dendrimer composite films upon vapor sorption C. R. Chim. **12**, 129, (2009).
[10] J. Chen, W.-F. Dong, H. Möhwald, R. Krastev: Amplified Fluorescence Quenching of Self-Assembled Polyelectrolyte-Dye Nanopartilces in Aqueous Solution Chemistry of Materials **20**, 1664, (2008).
[11] M. Delcea, R. Krastev, T. Gutlebert, D. Pum, U. B. Sleytr, J. L. Toca-Herrera: Mapping bacterial surface layers affinity to polyelectrolytes through the building of hybrid macromolecular structures J. Nanoscience and Nanotechnology **7**, 4260 , (2007).
[12] M. Delcea, R. Krastev, T. Gutlebert, D. Pum, U. B. Sleytr, J. L. Toca-Herrera: Thermal stability, mechanical properties and water content of bacterial protein layers recrystallized on polyelectrolyte multilayers Soft Matter **4**, 1414, (2008).

Replacement of Proteins by Surfactants from Adsorbed Interfacial Layers

Reinhard Miller 10.07.1950
1973: Diploma, Mathematics, (University of Rostock)
Thesis: Fredholm Operators
1977: Research Stay
(St. Petersburg University
with A.I. Rusanov)
1978: PhD, Physical Chemistry (Academy of Sciences, Berlin)
Thesis: Adsorption kinetics and exchange of matter of surfactants at liquid interfaces
1988: Habilitation, Physical Chemistry (Academy of Sciences, Berlin)
Thesis: Modelling of surfactants, surfactant mixtures and macromolecules at liquid interfaces
1990/91: NCERC Fellow
(University of Toronto with A.W. Neumann)
Since 1992: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)
2002: Research Stay
(NRC Lausanne with H. Watzke)

Thermodynamic and kinetic adsorption theories for mixed interfacial layers were derived by us recently, and the resulting equations of state, adsorption kinetics and dilational rheology were published for example in [1]. It was found for protein/surfactant mixed solutions that their adsorption at liquid interfaces is based on a combination of complex formation between protein and surfactant molecules and competitive adsorption between the formed complexes and free (unbound) surfactant molecules. The complexes are formed due to ionic and/or hydrophobic interactions between the different species. For non-ionic surfactants the complexes are formed exclusively on the basis of hydrophobic interactions between the surfactant's hydrocarbon chain and the hydrophobic domains of the protein **(Fig. 1,** top**)**. This results in more hydrophilic complexes which are less surface active than the original protein.
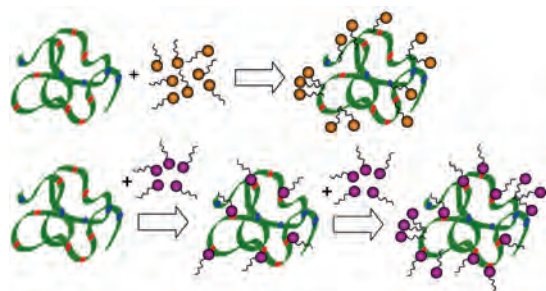

Fig. 1: Illustration of the interaction of surfactants and a protein molecule in aqueous solution; top – non-ionic surfactant, bottom – cationic surfactant; the red and blue areas on the protein chain represent negatively and positively charged domains, respectively.

The addition of ionic surfactants to a protein solution leads to complexes via the stronger ionic interaction between the charged surfactant head groups and the oppositely charged domains of the protein molecule. This process leads to increased hydrophobicity and hence higher surface activity of the complexes as compared to the original protein. Once the available charges in the protein chain are compensated, a further addition of surfactant molecules leads to hydrophobic interactions, hydrophilising the complexes, which become consequently less surface active **(Fig. 1,** bottom**)**. The interaction with surfactants causes conformational changes of the protein molecules in the bulk and at the interface.

The question whether proteins can be replaced by surfactants at an interface can be answered on the basis of this general mechanism. Experiments have been performed with various proteins, such as lysozyme [2, 3], β-casein (BCS) [4, 5], β-lactoglobulin (BLG) [6], and enzymes [7] in interaction with non-ionic surfactants like decyl and dodecyl dimethyl phosphine oxide ($C_{10}DMPO$ and $C_{12}DMPO$), fatty acid or monoglycerides, and ionic surfactants like sodium dodecyl sulphate (SDS) and dodecyl trimethyl ammonium bromide (DoTAB) at the water/air [2-5] and water/oil interfaces [6, 7].

Experimental surface tensions for mixtures of 7×10^{-7} mol/l lysozyme/SDS at different SDS concentrations are shown in **Fig. 2**. The isotherm for individual SDS solutions is also given for comparison. The curves correspond to calculations using the models given for example in [1]. The thin solid line corresponds to the formation of complexes by one protein molecule and 8 SDS molecules, assuming that the surface activity of the complex is the same as the one of the original protein molecule, while the bold solid line corresponds to an increase in surface activity of the complex by a factor of 10 [2].
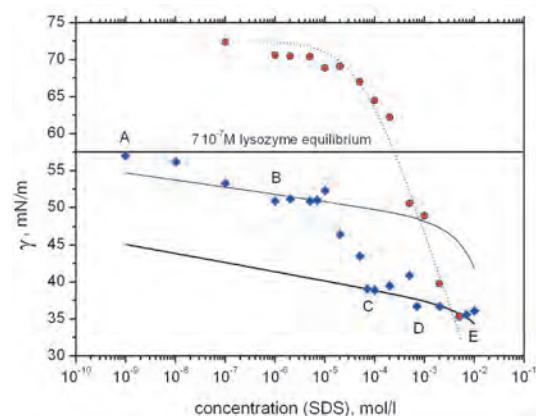

Fig. 2: Surface tension isotherm for SDS (♦) and 7×10^{-7} mol/l lysozyme + SDS (●) at the air/water interface, the lines are calculated curves as discussed in [2]

These two theoretical curves represent a kind of frame within which the experimental data are found. In the concentration range between the points A and B, electrostatic binding of SDS to the protein is very low in view of the low SDS/lysozyme ratio. At SDS concentrations higher than 10^{-6} mol/l (beyond point B) the electrostatic bonding of SDS becomes significant and the complexes are hydrophobised, resulting in an increased surface activity (BC range in **Fig. 2**). At pH 7 the net charge of lysozyme is about 8, so that charge neutralization can be assumed at about 5?10?5 mol/l SDS. Further increase in the SDS concentration leads to the hydrophilisation and stepwise solubilisation of the complex caused by the dominating hydrophobic interactions (CDE range); however, this does not result in a further significant surface tension change for the mixed solution.

The two measured isotherms, for the mixture and the pure SDS, overlap close to the critical micelle concentration of SDS (5×10^{-5} mol/l in buffer) suggesting an adsorption layer built mainly by free SDS molecules. The given explanations are confirmed by a decrease in the foam film thickness, by a decreased adsorbed amount, as measured by ellipsometry, and a change in the dilational rheological behaviour, which were all observed in the same concentration range [3].

The situation is changed when the protein molecules are pre-adsorbed and the adsorption of surfactants is made subsequently, as it was discussed recently [4]. In such a sequen-

tial adsorption process it is assumed that the proteins adsorb kinetically irreversibly, i.e. stay at the interface when all protein molecules are replaced from the subphase. Addition of the surfactant after another subphase exchange leads to a first contact and complex formation with the protein only at the interface.

In **Fig. 3** the dynamic surface tensions are shown as obtained in bulk-exchange processes with different surfactant concentrations, using a BCS layer pre-adsorbed from a 10^{-6} mol/l solution. The higher the surfactant concentrations, the lower are the final surface tensions. BCS, like most proteins with a molecular weight between 10 kDa and 30 kDa yields surface tensions not significantly lower than 50 mN/m. Thus, from the observed values, even below 30 mN/m, we can conclude that the surfactants displaced most of the protein molecules from the surface layer due to complexation and a subsequently strong competition.
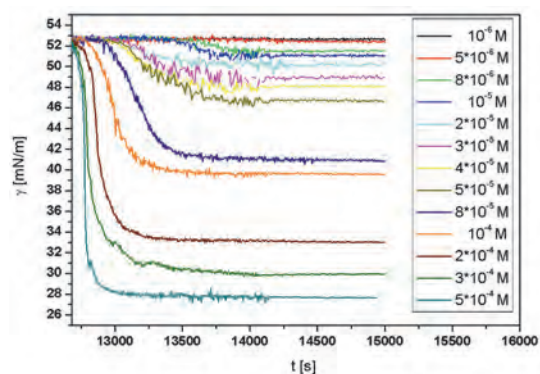

Fig. 3: Dynamic surface tensions measured during the drop-bulk exchange process measured for a sequential adsorption at different $C_{12}DMPO$ concentrations at a fixed BCS concentration of 10^{-6} mol/l [4]

In **Fig. 4**, surface tension curves are shown which correspond to another subphase exchange, replacing the previously injected $C_{12}DMPO$ molecules by a pure buffer solution (washing-out). In case, the surfactant has displaced the protein from the interface, we should arrive at a surface tension close to that of water, because any surfactant molecule desorbs immediately into a pure buffer solution. As one can see, the higher the injected $C_{12}DMPO$ concentration was, the closer are the final surface tensions to that of pure water, i.e. the more proteins were displaced from the interface by the surfactant molecules.
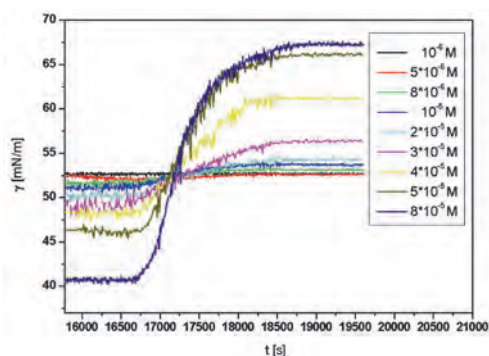

Fig. 4: Dynamic surface tensions measured during the drop-bulk exchange processes after sequential adsorption experiments at different $C_{12}DMPO$ concentrations and subsequent exchange with a buffer solution (washing out); all experiments were performed at an initial BCS concentration of 10^{-6} mol/l [4]

The displacement of protein molecules at the interface by increasing amounts of surfactants added to the bulk solution was also studied at the water/oil interface (water/hexane [6] and water/triglyceride [7]). As shown in **Fig. 5** for mixed BLG/SDS solutions, the adsorbed amounts of BLG are much higher at the water/hexane than at the water/air interface, while for the SDS the opposite is obtained. For SDS concentrations above 10^{-4} mol/l, the surface tensions for the mixtures at both interfaces decrease until the curves merge with the isotherm of the pure SDS and are identical at the CMC. Studies of dilational rheology indicate a decrease of the visco-elastic modulus at both interfaces which can again be attributed to the presence of an increasing quantity of surfactant molecules in the adsorption layer due to the replacement of the complexes [6].
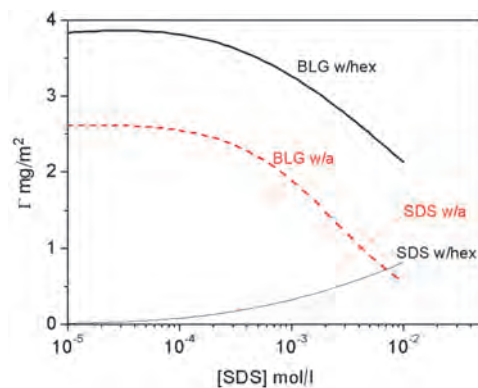

Fig. 5: Interfacial concentration Γ of BLG and SDS adsorbed at the water/air (dash line) and the water/hexane (solid line) interface, calculated from $\gamma(c)$ isotherms [6]

R. Miller, V.S. Alahverdjieva, A. Javadi, J. Krägel, Cs. Kotsmár, V. Pradines, E. Santini, S. Siegmund, D. Vollhardt (in close cooperation with E.V. Aksenenko, V.B. Fainerman, D.O. Grigoriev, V.I. Kovalchuk, M.E. Leser and B.A. Noskov)
miller@mpikg.mpg.de

References:

[1] Fainerman, V.B., Kovalchuk, V.I., Leser, M.E. and Miller, R.: Effect of the intrinsic compressibility on the dilational rheology of adsorption layers of surfactants, proteins and their mixtures, in "Colloid and Interface Science Series", Th. Tadros (Ed.), Vol.**1**, Wiley, 307-333 (2007).

[2] Alahverdjieva, V.S., Fainerman, V.B.: Aksenenko, E.V., Leser, M.E. and Miller, R., Adsorption of hen egg-white lysozyme at the air-water interface in presence of sodium dodecyl sulphate, Colloids Surfaces A **317**, 610-617 (2008)

[3] Alahverdjieva, V.S., Grigoriev, D.O., Fainerman, V.B., Aksenenko, E.V., Miller, R. and Möhwald, H.: Competitive adsorption from mixed hen-egg white lysozyme/surfactant solutions at the air water interface studied by tensiometry, ellipsometry and surface dilational rheology, J. Phys. Chem. B. **112**, 2136-2143 (2008).

[4] Kotsmar, Cs., Grigoriev, D.O.: Makievski, A.V., Ferri, J.K., Krägel, J., Miller, R. and Möhwald, H.: Drop profile analysis tensiometry with drop bulk exchange to study the sequential and simultaneous adsorption of a mixed β-casein /C_{12}DMPO system, Colloid Polymer Sci. **286**, 1071-1077 (2008)

[5] Kotsmar, Cs., Arabadzhieva, D., Khristov, Kh., Mileva, E., Miller, R. and Exerowa, D.: Adsorption Layer and Foam Film Properties of Mixed Solutions Containing β-casein and C_{12}DMPO, Food Hydrocolloids **23**, 1169–1176 (2009).

[6] V. Pradines, J. Krägel, V.B. Fainerman and R. Miller: Interfacial properties of mixed β-lactoglubulin-SDS layers at the water/air and water/oil interface, J. Phys. Chem. B, **113**, DOI: 10.1021/jp8091573 (2009).

[7] Reis, P., Holmberg, K., Miller, R., Krägel, J., Grigoriev, D.O., Leser, M.E. and Watzke, H.J.: Competition between lipase and monoglycerides at interfaces, Langmuir **24**, 7400-7407 (2008).

Ion Distribution at Interfaces

Hubert Motschmann 30.05.1961

1988: Diploma, Chemistry
(University of Erlangen)
Thesis: Numerical and analytical
studies on the quantum dynamical
equation of Davidov Solitons

1991: PhD, Chemistry
(Max Planck Institute of
Polymer Research, Mainz)
Thesis: Scaling and adsorption
studies of Block-copolymers

1991-1993: Postdoc
(Eastman Kodak, Rochester, New York)

Since 1994: Group Leader
(Max Planck Institute of Colloids
and Interfaces, Potsdam)

Since 2008: Professor
(Physical Chemistry University of
Regensburg)

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

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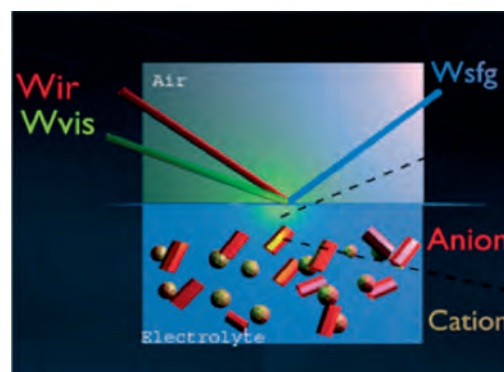

Fig. 1: Scheme of a SFG experiment: The spatial and temporal overlap of an infrared and visible laser pulse generates light at the sum frequency.

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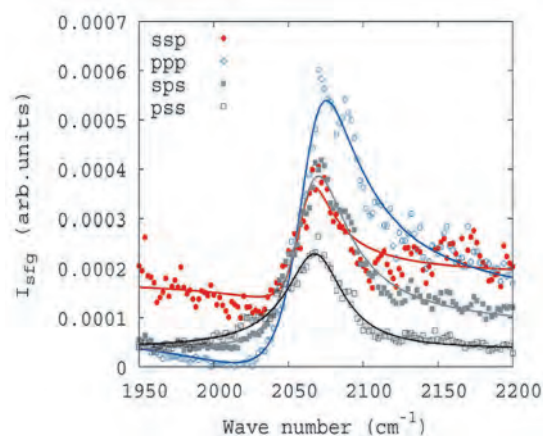

Fig. 2: Vibrational sum frequency spectra showing the CN stretch of the thiocyanate anion for 1~M potassium thiocyanate solution. The points and continuous lines represent the experimental data and fits respectively.

Polarization dependent measurements have been used for a determination of the orientation of the pseudo-halide anion. The combined data gives a picture of the interfacial architecture on a molecular scale. We believe our current study contributes towards better understanding of this biologically relevant chaotropic ion and water interactions at the interface. Further our work shows that the orientation of the anion is relevant and needs to be taken into account to get a full picture on the interfacial architecture.
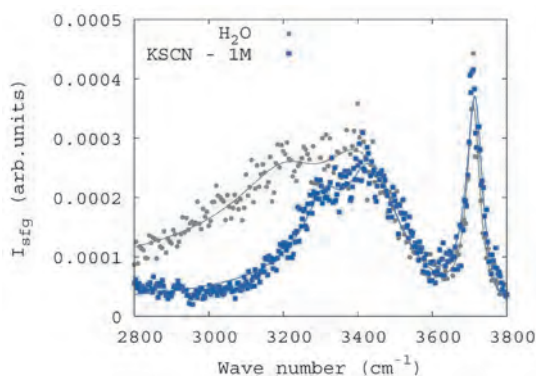
Fig.3 Vibrational sum frequency spectra of water and 1 ~M potassium thiocyanate solution. The points and continuous lines represent the experimental data and fits, respectively.

As a consequence of its chaotropic nature, the favourable adsorption of the thiocyanate anion at the interface perturbs the hydrogen bonded network and distorts it significantly which becomes more prominent at higher concentration. In particular, the spectra show considerable enhancement of liquid-like ordering occurring at 3450 cm^{-1} and vanishing ice-like feature at 3200 cm^{-1} in agreement with recent reports on large and highly polarisable anions. In addition, the feature at 3320 cm^{-1} which is attributed to the tetrahedral coordination of water increases with concentration. The geometry of the thiocyanate anion (linear), higher polarizability and its low hydration tendency in addition to its orientation, clearly restructures the water network at the interface. Molecular dynamics simulation would shed some light on the density of the dominant species at the interface and the nature of ion-water interactions by constraining the orientation of the ion. Understanding of this mechanism of hydration will be crucial to address the more complex protein-aqueous electrolyte interfaces concerning the "salting in" and "salting out effects", specifically to identify whether direct ion-protein local binding or mediation through interfacial water are responsible for such processes.

The reported features are not a peculiarity of the thiocyanate. For instance we could prove that potassium azid behaves in a very similar fashion. Another interesting system which we recently studied is the potassium hexacyanoferrat **(Fig. 4)**. This inorganic complex possesses octahedral symmetry Oh. A normal coordinate analysis reveals that this model system does not possess SFG active modes.
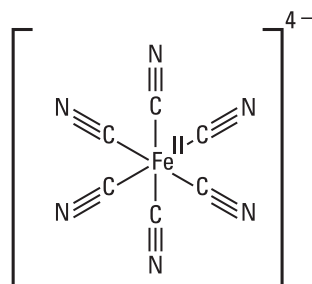

Fig. 4: Structure of the hexacyanoferrate ion

However, we detect a strong IR-VIS SFG signal for the ssp polarisation combination in reflection mode at the air-water interface **(Fig. 5)**. The asymmetry of the interface apparently deforms the octahedral coordination shell from oh to C4v symmetry and distinct vibrational modes can be observed in the spectra.
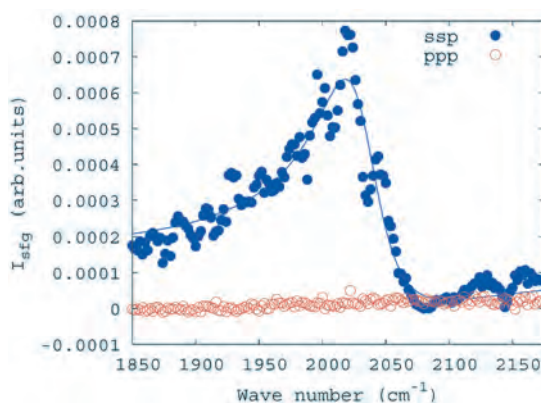

Fig. 5: Vibrational sum frequency spectra of the hexacyanoferrate ion at the air/water interface for two different polarizations.

This work must have also impact on atmospheric research and it is on the agenda to explore this. It is well established that some electrolytes at sufficiently high concentration can inhibit bubble coalescence relative to the pure liquid. V. Craig et al. classified electrolytes according to their coalescence behaviour based on empirical cation and anion assignments. The mechanism behind electrolyte inhibition, as well as the salt differentiation, is not understood but must be related to the internal organization at the interface.

Hubert Motschmann, P. Viswanath, P. Karageorgiev
hubert.motschmann@mpikg.mpg.de

References:
[1] P. Viswanath, H. Motschmann: Oriented Thiocyanate Anions at the Air-Electrolyte Interface and Its Implications on Interfacial Water – A Vibrational Sum Frequency Spectroscopy Study. Journal of Physical Chemistry **111**, 4484-4486, (2007)
[2] P. Koelsch, P. Viswanath, H. Motschmann, V.L. Shapovalov, G. Brezesinski, H. Möhwald, Dominik Horinek , R. Netz, K. Giewekemeyer, T. Salditt, H. Schollmeyer, R. v. Klitzing, Jean Daillant , Patrick Guenoun: Specific ion effects in pysicochemical and biological systems: Simulations, theory and experiments. Colloids and Surfaces A: Physicochem. Eng. Aspects **303** (1-2): 110-136 AUG 1 (2007)
[3] M. Zharnikov, T. Weidner, F. Bretthauer, N. Ballav, H. Motschmann, H. Orendi, H., C. Bruhn, U. Siemeling: Correlation between the molecular structure and photoresponse in aliphatic self-assembled monolayers with azobenzene tailgroups. Langmuir **24**, 11691, (2008)
[4] P. Viswanath, H. Motschmann: Effect of interfacial presence of oriented thiocyanate on water structure. Journal of Physical Chemistry C **112**(6), 2099 (2008).
[5] S. Schmidt, H. Motschmann, T. Hellweg, R. von Klitzing: Thermoresponsive surfaces by spin-coating of PNIPAM-co-PAA microgels: A combined AFM and ellipsometry study. Polymer **49**(3):749-756, (2008).

SOLID INTERFACES

Phase Transitions, Nucleation, and Transport Phenomena at Solid/Air Interfaces

Hans Riegler 29.01.1955
1982: Diploma, Physics,
(Würzburg University)
Thesis: Light-induced drift of CHF3
1986: PhD, Physics
(Munich, Technical University)
Thesis: Protein/lipid-interactions of
photosynthetic reaction centers and
Cytochrome C in model membranes.
1986-1988: Postdoc, AT&T Bell Laboratories, Princeton, NJ, USA
1988-1995: Group Leader, Institute of
Physical Chemistry, (Mainz University)
Since 1995: Group Leader,
(Max Planck Institute of Colloids
and Interfaces, Potsdam)
1996: Habilitation, (Mainz University)
Thesis: Interface-induced structure formation through Langmuir-wetting in
monomolecularly thick organic layers
on planar solid surfaces

Aims:

Understanding of solid/liquid phase transitions, nucleation, structure formation, transport phenomena, and wetting properties of confined systems, in particular molecularly thin films at solid/air interfaces.

In fundamental science these processes are important in the early stages of solidification/melting (nucleation, cluster formation) as well as (non-equilibrium) bulk aggregation. In applied science our research is relevant for 2-dimensional systems or systems with small dimensions, e.g. in microfluidics, nanotechnology, sintering, etc.

Work:

In the last two years we gained new insights into:

1.) *How the surrounding interface affects the solid/liquid phase transition behavior of adsorbed solid aggregates.* We find that the wetting properties of surrounding interfaces can considerably lower (up to more than 50 °C!) the solid/liquid phase transition of adsorbed aggregates. For the investigations we use a specially developed optical interference enhanced microscopy technique.

2.) *How line tension affects the shape of adsorbed solid aggregates.* High resolution AFM shows that the contact angle of nano-sized sessile droplets (solid aggregates) of C60 decreases with size. This is an indication for a negative line tension.

3.) *How the interfacial properties affect (delay) the coalescence behavior of sessile droplets.* Contrary to intuition sessile droplets of completely miscible liquids do in many cases not fuse instantaneously upon contact. This delay in droplet fusion is caused by surface flow due to interfacial tension gradients.

Details:

Molecules, which form layered structures in their solid phase (long chain alkanes, alcohols, fatty acids, etc.) show an amazing variety of different topologies (droplets, domains, films, layers, terraces …) if they are deposited as molecularly thin films at solid/gas interfaces. These topologies depend on surface coverage, temperature, and preparation history as exemplified in **Fig. 1** with $C_{30}H_{62}$ at SiO_2/air-interfaces:

Above $T > T_{sf}$ (sf = "surface freezing") all alkane is molten. It forms a completely wetting film of uniform thickness.

Below T_{sf} the alkane forms a single solid monolayer adjacent to the solid surface ("surface freezing"). If the overall coverage is not sufficient to form a complete solid monolayer ("submonolayer coverage"), monolayer domains coexist with a submonolayer of individual alkane molecules. The alkane distribution between monolayer domains and submonolayer varies with temperature and reveals details on the interfacial interactions (see **Fig. 1**).
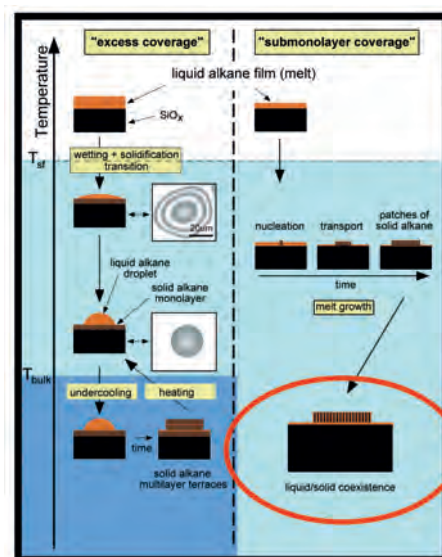

Fig. 1: Various alkane film topologies as a function of coverage and temperature. We find that this phase/topology diagram is generic and valid for many rod-like molecules. Currently our research activities focus on the equilibrium coexistence of monolayer domains and liquid film.

If the alkane coverage exceeds one monolayer ("excess coverage") liquid bulk droplets coexist with the frozen monolayer. Below the bulk melting temperature T_{bulk} these droplets solidify and form multilayers of solid lamellae.
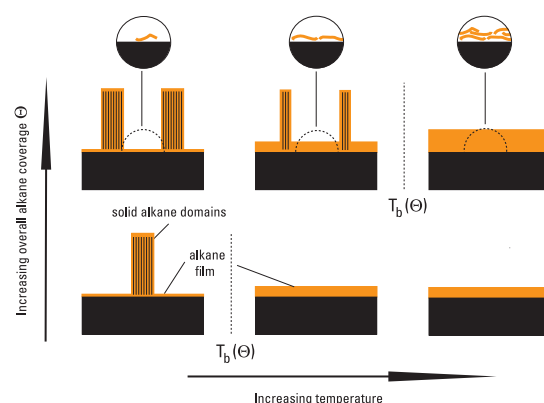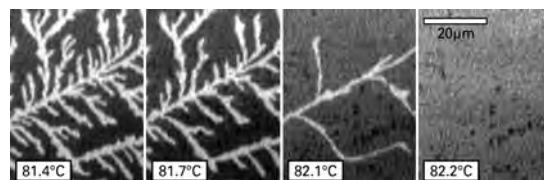

Fig. 2: Partial melting of C40 domains upon temperature increase (top). Schematic of the coexistence of solid domains with a liquid film as function of temperature and overall deposited amount of molecules. This behavior is generic for many molecules (see Fig. 3).

Meanwhile it has been shown that these various phases/ topologies are generic for many rod-like molecules. There are still many open fundamental questions like: Do the wetting and the surface freezing point at T_{sf} coincide? What is the molecular ordering at the interface between the liquid droplet and interface between T_{sf} and T_b? What are the transport properties of the molecules in the submonolayer or above the frozen monolayer?

The temperature dependence of the alkane partitioning between domains and submonolayer film gives new insights into the properties of the submonolayer film (e.g., it behaves like a 2d gas). **Fig. 2** shows a schematic of the partial, gradual melting of C40 domains as the temperature is increased and a sketch revealing the relation between overall surface coverage and temperature of complete melting of the solid domains ($T_b(\Theta)$). This general behavior has now also been observed for long chain alcohols **(Fig. 3)** corroborating the general relevance of the scheme of **Fig. 1**.
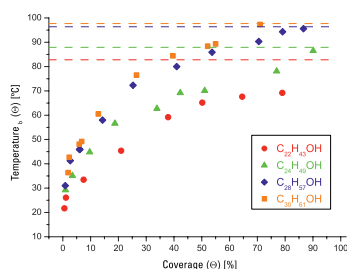

Fig. 3: Temperature of complete melting of long chain alcohol domains ($T_b(\Theta)$, see Fig. 2) as function of the coverage Θ (in % of complete monolayers, dashed lines = melting temperature of a complete monolayer ($T_b(\Theta=1)$.

We also investigate the question of the magnitude and the sign of line tension, which has been under discussion since its first mentioning by Gibbs about a century ago. **Fig. 4** shows that very low coverages of SiO_2/air-interfaces with C60 leads to nano-sized sessile C60 droplets (contact area diameter $\ll$ 100 nm). With these droplets we could image directly the impact of line tension on the droplet topology. Smaller droplets show a smaller contact angle indicating a negative line tension of about -10e-11 N. The data suggest a crossover from 3-dimensional domains at contact areas below 10 nm radius. This crossover and the existence of such small 2-dimensional domains are currently under investigation. It would give new insights into understanding nucleation.
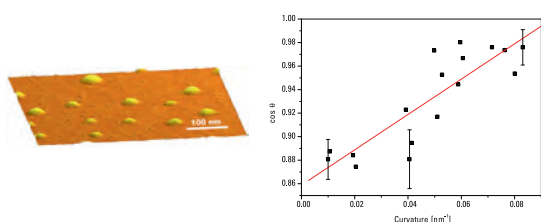

Fig. 4: Nano-sized C60 droplets and their contact angles as function of the curvature (size).

Another project investigates the influence of interfacial interactions on the fusion of (macroscopic) droplets of completely miscible liquids. Quite unexpected, sessile droplets of completely miscible liquids do not fuse instantaneously after contact (both, capillary and volume free energy favor fusion!). Instead, after a first contact, a liquid film/bridge is formed between the droplets **(Fig. 5)** and they repel each other and move over the surface („chasing" droplets). Supposedly this separation is stabilized by flows driven by surface-tension gradient between the two liquids (Marangoni-effect).
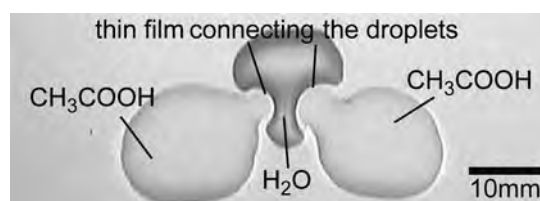

Fig. 5: Delayed fusion between droplets of completely miscible liquids.

Future Plans:

In the future the investigations on the influence of the interface on phase transitions and 2d transport phenomena will be extended to other rod-like substances (fatty acids, short polymers, liquid crystalline materials) as well as other planar substrates (TiO_2, etc.) to work out the more general aspects of the findings.

We will also focus more on the early stages of phase transitions, on molecularly-sized 2d and 3d aggregates and nucleation. Our system is well-suited to specifically investigate the various interfacial influences ("active" interfacial sites) on nucleation and growth). We will investigate the nucleation (growth) of 2d as well as 3d systems. In the latter case we may use the fairly well specified, self-organizing 2d (fractal) domain patterns as templates to investigate the nucleation and growth of 3d systems (a simple example: water condensation on these surfaces).

We will investigate the reasons why the 2d films solidify in certain structures (e.g., fractal 2d domain shapes, terraces, etc.) or what determines the shape of molecularly sized 3d structures (e.g. the influence of line tension on droplet shape). The findings will be used to build optimized structures for organic hetero-junction photovoltaic cells in a collaborative project with academic and industrial partners.

In addition we will investigate the transport properties of 2d systems (the molecular transport in submonolayer films) in an international graduate school with TU Berlin.

Hans Riegler
hans.riegler@mpikg.mpg.de

References:
[1] H. Riegler and R. Köhler, Nature Physics **754**, (2007).

[2] H. Riegler and Paul Lazar, Langmuir **24**, 6395 (2008).

From Molecular Modules to Modular Materials

Dirk G. Kurth 06.11.1964

1990: Diploma, Chemistry
(RWTH-Aachen)
Thesis: Preparation, characterization
and reactivity of molecular monolayers
on metal oxide substrates.

1993: PhD, Chemistry
(Purdue University)
Thesis: Synthesis, Reactivity, and
Characterization of Thin Organic
Films on Metallic Substrates

1994-1996: Postdoc
(Université Louis Pasteur, Strasbourg)

Since 1996: Group Leader
(Max Planck Institute of Colloids
and Interfaces, Potsdam)

2003: Habilitation (Potsdam)
Thesis: Self-Assembly of Hierarchically
Structured Architectures of Metallo-
supramolecular Modules

Since 2004: Director National
Laboratory for Materials Science
(NIMS), Tsukuba, Japan.

Since 2008: Professor
(University Würzburg)
Chemische Technologie der
Materialsynthese

Within the last decades, self-assembly as principle in material science has gained considerable importance and attracted increasing attention in chemistry, physics, and material science. In comparison to traditional material manufacturing self-assembly has potential advantages, such as parallel production, molecular dimension control, defect tolerance, self-repair, and increased life-time. The modularity offers synthetic simplicity and rapid adaption to specific needs. Considering the energies involved self-assembly can be envisioned as key technology in sustainable and environmentally safe fabrication, relying on aqueous media predominantly.

Starting from readily accessible components, self-organization allows tailoring the final material architecture through the judicious design of the building blocks and interactions. The principles of self-assembly are inspired by nature, based on weak and competing interactions, such as hydrogen bonding, metal ion coordination, van der Waals interactions, as well as reversible covalent bonds including esters, disulfides, and cycloadditions. Where biological systems continually demonstrate the delicate control on all levels of the architecture to influence structure and function, material science is still in progress of unraveling the *Aufbaurules* for self-assembly of hierarchical architectures.

Materials built up through weak interactions exhibit under ambient conditions dynamic behavior, including assembly, disassembly and reconstruction. In addition, these materials can be adaptive and responsive to external triggers, such as temperature, pH, solvent, ionic strength or external fields. These phenomena are unavailable in classical materials based on covalent bonds.

Our interest focuses on the investigation of the underlying principles of self-assembly in complex systems such as metallo-supramolecular coordination polyelectrolytes and architectures based on these polymers.

While the characterization and investigation of kinetically inert transition-metal complexes can be conducted by standard analytical methods, the investigation of dynamic polymeric assemblies formed by kinetically labile transition-metal complexes has remained challenging. Due to the enormous prospects of dynamic polymers, we have taken a detailed look at the formation, self-assembly, structure and properties of dynamic macromolecular assemblies using ditopic bis-terpyridine ligands, e.g. 1,4-bis(2,2′:6′, 2′′-ter-pyridine-4′-yl)benzene **(tpy-ph-tpy)** and kinetically labile transition metal ions including Fe(II), and Ni(II).

The ability to tune the binding affinity by choosing the appropriate metal ion and ligand as well as the well-defined stereochemistry of complexes makes these building blocks promising candidates for the assembly of dynamic and functional metallo-supramolecular coordination polyelectrolytes (MEPEs) **(Scheme 1) [1, 2]**. The synthetically appealing preparation and the readily availability of MEPEs has stimulated research concerning the embedding of MEPEs in meso-porous materials **[3]**, Layer-by-Layer thin films **[2]**, electro-chromic **[4]**, and magnetic materials **[5]**.
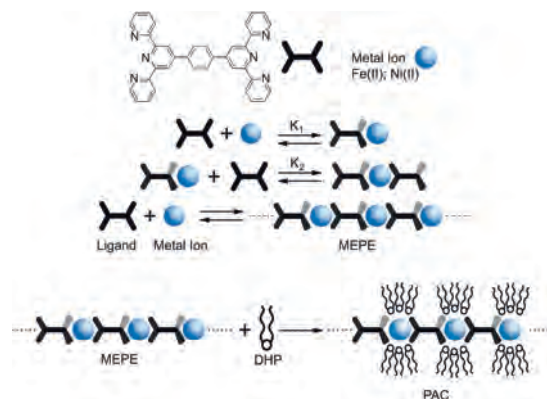
Scheme 1: Metal ion-induced self-assembly of Fe(II) or Ni(II)acetate and 1,4-bis(2,2′:6′, 2′′-terpyridine-4′-yl) benzene **(tpy-ph-tpy)** leads to positively charged metallo-supramolecular coordination polyelectrolytes (MEPE). The binding constants of terpyridine and first row transition metal ions are large enough to support macroscopic dynamic assemblies. Due the charge MEPE are soluble in aqueous media. The coordination geometry and the design of the ligand result in a rigid-rod type structure. Self-assembly occurs in two steps (middle), the binding of a metal ion and a ligand followed by coordination of a second ligand under formation of the bis-terpyridine complex. Each assembly step is characterized by a binding constant K_1 and K_2. Sequential self-assembly with amphiphiles such as dihexadecyl-phosphate (DHP) results in the corresponding polyelectrolyte-amphiphile complexes (PAC), which can be incorporated into extended architectures such as Langmuir-Blodgett films.

The molar mass distribution of MEPE depends on the total concentrations, the stoichiometry of the constituents as well as external parameters such as pH, solvent and temperature. In a first approximation, the self-assembly of MEPEs and their dynamic equilibrium of association and dissociation is based on the law of mass action. Following this principle we developed a theory that allows us to describe and predict the molar-mass distribution of MEPE as a function of experimental parameters. The theory predicts an exponential growth of MEPE as a function of concentration if the stoichiometry of ligand and metal ion is one. Notably, the stoichiometry has a strong impact on the average molar mass **(Fig. 1)**.
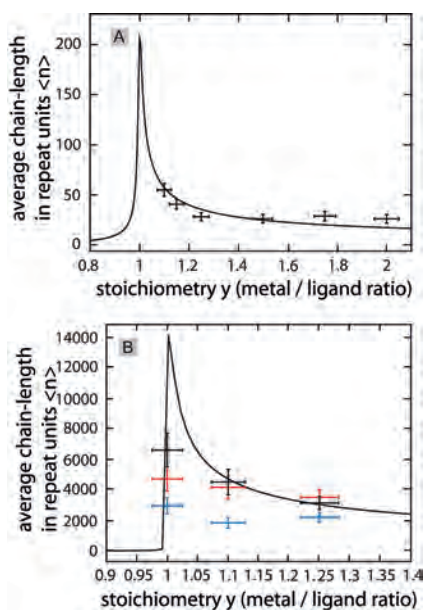
Fig. 1: Average number of monomers per chain <n> as a function of stoichiometry, y, for MEPE assembled from tpy-ph-tpy and Ni(II) (A) and Fe(II) (B), respectively. The concentration was kept constant during the measurement. Symbols resemble AUC measurement, while lines show fitting curves obtained by our theoretical model. The samples were equilibrated for different times: A) one sample equilibrated for 28 days, including fit and error bars, indicated by size of the symbols. B) blue for 1 day, red for 2 days, black for 9 days, a fit could only be obtained for the longest equilibration time; the error of measurement is indicated by the size of the symbols. Here, the stability constants of Fe(II, Ni(II)) and terpyridine are used ($log[K_1] \ll log[K_2]$).

Starting from ligand excess, the stoichiometry curves (Ni-MEPE **Fig. 1A** and Fe-MEPE **Fig. 1B**) show a steep increase in average molar mass as the stoichiometry, y, approaches one. Apparently, only small assemblies are present in solution in this regime, which self-assemble abruptly when the ligand and metal ion concentrations converge. Above the 1:1 stoichiometry the average molar mass gently decreases and approaches an almost constant value. Notably, even if an excess of metal ions is present in the solution, macromolecular assemblies are formed because K_2 is much larger then K_1 and therefore the equilibrium is on the side of macromolecular species. In contrast, an excess of ligand results in small assemblies presumably mostly dimeric species, consisting of two ligands and a metal ion, which are favorable due to large K_2 value. As a result, we observe a strong asymmetry in the curve of the average molar mass in close proximity to 1:1 stoichiometry. The abrupt change can be envisioned to be used in rheology to open an avenue for the construction of smart materials, e.g. if the stoichiometry is manipulated by an external trigger.

These findings were confirmed by viscosity measurements and molar mass determination using analytical ultracentrifugation. Not surprisingly we also find that MEPE solutions are thixotropic, another property of technological interest.
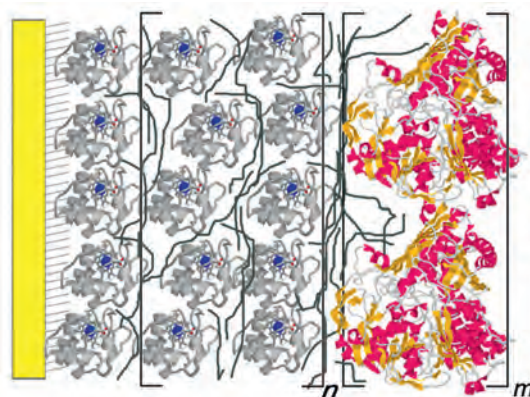

Fig. 2: Scheme of the two protein multilayer assembly for superoxide (O_2^-) detection. A cytochrome C **(cyt c)** monolayer is formed on MUA/MU (1:3) modified gold electrodes. The cyt c multilayer is built by alternating incubations in PASA and cyt c solutions. Finally, multilayers of PEI/XOD are assembled on the surface.

Other areas of interest include structure-property relationships in functional materials based on polyoxometalate clusters **[6]** and fullerenes **[7]** as well as the application of self-assembled architectures in bio-molecule mediated sensing **[8, 9]**. We demonstrated that a sensor carrying a thin film built-up by Layer-by-layer technique and composed of cytochrome C, polyaniline sulfonic acid (PASA) in combination with xanthine oxidase is effectively detecting and measuring superoxide in solution **(Fig. 2) [8]**.

D. G. Kurth, V. A. Friese, R. Dronov, N. Miyashita, G. Schwarz, T. K. Sievers, A. Vergin.
dirk.kurth@matsyn.uni-wuerzburg.de

References:
[1] Sievers, T.K., Vergin, A., Möhwald, H., Kurth, D.G.: Thin films of cross-linked metallo-supramolecular coordination polyelectrolytes Langmuir, **23**, 12179 (2007).
[2] Friese, V.A., Kurth, D.G.: Soluble dynamic coordination polymers as a paradigm for materials science Coord. Chem. Rev., **252**, 199 (2008).
[3] Akcakayiran, D., Mauder, D., Hess, C., Sievers, T.K., Kurth, D.G., Shenderovich, I., Limbach, H.H., Findenegg, G.H.: Carboxylic Acid-Doped SBA-15 Silica as a Host for Metallo-supramolecular Coordination Polymers J. Phys. Chem. B, **112**, 14637 (2008)
[4] Han, F.S., Higuchi, M., Kurth, D.G.: Metallo-supramolecular polymers based on functionalized bis-terpyridines as novel electrochromic materials. Adv. Mater., **19**, 3928 (2007).
[5] Bodenthin, Y., Kurth, D.G., Schwarz, G.: On the memory chip of tomorrow? Spin-transitions in the supra-molecular structure. Chemie in unserer Zeit, **42**, 256 (2008)
[6] Wu, P., Volkmer, D., Bredenkotter, B., Kurth, D.G., Rabe, J.P.: Isolated and linear arrays of surfactant-encapsulated polyoxometalate clusters on graphite. Langmuir, **24**, 2739 (2008)
[7] Nakanishi, T., Ariga. K., Michinobu, T., Yoshida. K., Takahashi, H., Teranishi, T., Möhwald, H., Kurth, D.G.: Flower-shaped supra-molecular assemblies: Hierarchical organization of a fullerene bearing long aliphatic chains. Small, **3**, 2019 (2007)
[8] Dronov, R., Kurth, D.G., Möhwald, H., Scheller, F.W., Lisdat, F.: A self-assembled cytochrome c/xanthine oxidase multilayer arrangement on gold, Electrochim. Acta, **53**, 1107 (2007).
[9] Dronov, R., Kurth, D.G., Möhwald, H., Scheller, F.W., Lisdat, F.: Communication in a protein stack: Electron transfer between cytochrome c and bilirubin oxidase within a poly-electrolyte multilayer. Angew. Chem., Int. Ed., **47**, 3000 (2008)

Nanotechnology for Bio-Applications

Andre G. Skirtach 22.10.1967
1993: Diploma, Physics
(Moscow State University of
Lomonosov, Moscow, Russia).
Thesis: Numerical Modeling
of Ultrathin Domain Walls.
1997: PhD, Physical Chemistry
(McGill University, Montréal, Canada).
Thesis: Optical Wavemixing in Nonlinear Absorptive Kerr Media.
1997-2000: Associate Research Officer
(National Research Council/Conseil
national de recherches du Canada,
Ottawa, Ontario, Canada).
2000-2002: Co-establishing prominent
start-up Trillium Phot. Inc.
(Ottawa, Ontario, Canada).
Since 2003: Researcher
(Max-Planck Institute of Colloids
and Interfaces, Potsdam).

The research group of nanotechnology for bio-applications uses the methods of nano-technology for understanding processes relevant to biology and other fields. The aim is to advance in understanding of fundamental processes and use this knowledge for development of practical applications. One direction is devoted to development of advanced drug delivery vehicles and planar membranes with remote release capabilities for studying intracellular processes in the areas of immunology and protein science. Self-assembly of nanoparticles on both spherical particles and planar surfaces, thermal properties on the nano-scale are also in focus. In addition, novel materials with advanced optical and opto-electronic properties are investigated.

The group's goals are:
· understanding intracellular transport of small peptides;
· development of drug delivery vehicles for studying functions and conformation states of proteins;
· research in the area of nano-manipulations at the polymer-water and polymer-air interfaces;
· thermal properties of polymers and localized permeability control of membranes, films, polymers, etc. at the nanometer scale;
· materials with novel optical and opto-electronic properties.

Intracellular processes provide important information for immuno-response of the system, neurological disorder etc. Studying intracellular processes is hindered by intricacy of non-invasive access to the interior of living cells.

Using polymeric capsules and remote release methods, we have recently introduced remote and non-invasive methods of release of encapsulated materials inside living cells. **Fig. 1** demonstrates that a microcapsule filled with fluorescently labeled molecules is up-taken by a living cell. The walls of the capsule are functionalized with nanoparticles which absorb light energy and convert it to heat. In addition to nanorods, spherical nanoparticle aggregates produce absorption in the "bio-friendly" near-IR (infrared) part of the spectrum. The aggregation of nanoparticles can be induced either by concentration or by shielding the stabilizers on the nanoparticles. Local, nanometer-size, heating by a biologically friendly near-IR laser light affects the permeability of the outer polymeric shell allowing materials to be released remotely. The feasibility of release inside living cells was recently shown. This enables studying various intracellular processes triggered at a desired point in space and time.

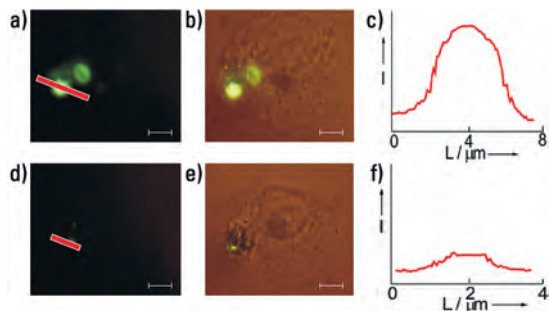The principles of remote release are also looked at for controlling the permeability of membranes.

Fig. 1: Sequence of images showing the release of fluorescent AF-488 dextran inside a living MDA-MB-435S cancer cell.
a) Fluorescence image of a filled capsule; b) both transmission and fluorescence images of the capsule inside the same cell;
c) fluorescence intensity, I, profile plotted along the red line in a).
Figure 1 d) - f) present similar data after exposing the cell to a laser beam. The scale bars in all images correspond to 5 µm.

Fig. 2 presents remotely controlled nanometer scale polymeric membranes. The remote action is achieved by exposing the membrane functionalized with absorbing nanoparticles to a laser beam. The nanoparticles locally affect the permeability of polymeric membranes increasing it transiently under the action of the laser beam, and thus allowing molecules to pass through. This "smart" membrane seals itself after laser illumination is switched off. The process is repeatable as the membrane can be re-activated again with another laser exposure. Controllable membranes are expected to find application in various areas from separation chemistry to neurology.
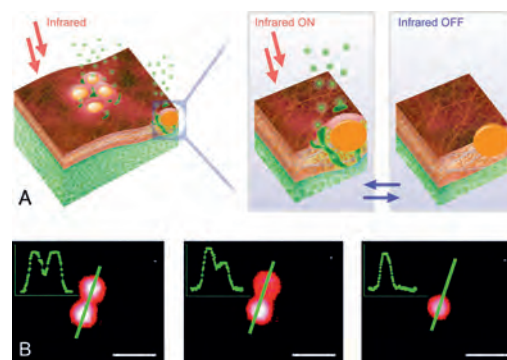
Fig. 2: Remote release from microcapsules. (A) Schematics of nanoparticle functionalized polymeric nanomembranes opening channels upon laser illumination. (B) A polymeric microcapsule shell acts as a reversible nanomembrane. Upon laser light illumination the microcapsule (left image) partially releases encapsulated polymers and reseals (middle). After the second illumination the microcapsule completely releases its content (right).
Profiles in the left upper corner are drawn along the green line.
Scale bars in all images correspond to 5 µm.

Near-IR absorption can be induced either by nanorods or by aggregates of spherical nanoparticles. In the case of citrate-stabilized nanoparticles, aggregation can be induced by screening charges on the nanoparticles **(Fig. 3)**. On the other hand, the non-aggregated state of nanoparticles can be obtained by direct adsorption at low concentration.
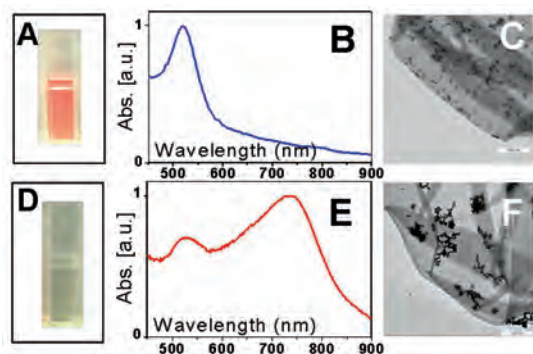

Fig. 3: A solution of citrate-stabilized gold nanoparticles has a red color as seen through a plastic cuvette (A). Its corresponding UV/Visible absorbance spectrum shows a strong absorbance peak at 520 nm (B), TEM image of dry (PDADMAC/Au/PSS)₄ shells with non-aggregated gold particles (C). The color of the gold solution after adding salt is blue/gray (D), its corresponding absorption spectrum (E) and the general appearance of these aggregates as seen when inserted in the wall of (PDADMAC/Au/PSS)₄ microcapsule (F). Scale bars in TEM images correspond to 500 nm.

The temperature rise on the nanoparticles is the key mechanism that affects the permeability of polymeric membranes. Controlling the distribution of nanoparticles effectively determines the temperature distribution upon laser light illumination. Aggregation of nanoparticles enhances the temperature rise around them; in case of near-IR illumination this effect is enhanced because of increased absorption of nanoparticle aggregates in the near-IR part of the spectrum.
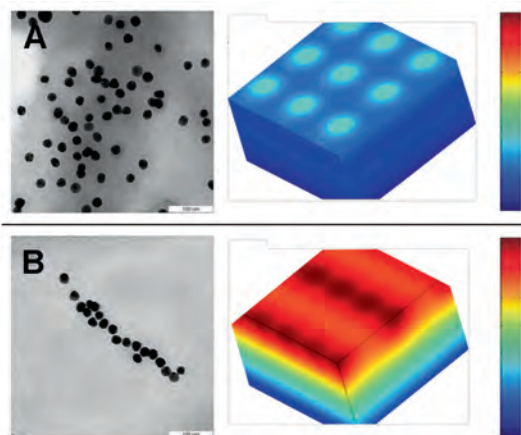

Fig. 4: TEM images (left-hand side) of uniform or non-aggregated (A) and aggregated (B) distribution of nanoparticles. Modelling (right-hand side) of the temperature rise around nanoparticles. Non-aggregated nanoparticles without near-IR laser, (A), are shown together with aggregated nanoparticles illuminated by a near-IR laser, (B). For 20 nm nanoparticles the absorption coefficient at ~ 800 nm is about 0.02, so the temperature rise at 50 mW of incident power of a focussed laser operating at 830 nm is less than 1 degree. For a single line of four aggregated nanoparticles the same conditions lead to the temperature rise of 7 K can (red color). The scale bars in the TEM images are 100 nm.

Future Tasks:

· Investigation of small peptide presentation at the cellular surface relevant to immunology (with Jacobs University Bremen).
· Looking at the functions and structures of proteins inside living cells (with Max-Planck Institute for Biophysical Chemistry, Göttingen).
· Studying thermal properties of ultrathin membranes on the nanoscale.
· Nanoparticle self-assembly at the polymer-water interface for remotely activatable, biocompatible planar thin films/particles and for renewable energy applications.
· Novel materials with optical and opto-electronic properties.

A. G. Skirtach, M. F. Bedard, and H. Möhwald
skirtach@mpikg.mpg.de

References:
[1] Bedard, M. F., Braun, D., Sukhorukov, G. B., Skirtach, A. G.: Toward Self-Assembly of Nanoparticles on Polymeric Microshells: Near-IR Release and Permeability. ACS Nano **2**, 1807 (2008).
[2] Skirtach, A. G., Karageorgiev, P., Bedard, M. F., Sukhorukov, G. B., Möhwald, H.: Reversibly Permeable Nanomembranes of Polymeric Microcapsules. J. Am. Chem. Soc. **11**, 11572 (2008).
[3] Skirtach, A. G., Karageorgiev, P., De Geest, B. G., Pazos-Perez, N., Braun, D., Sukhorukov, G. B.: Nanorods as Wavelength-selective Absorption Centers: Visible and near-IR part of the spectrum. Adv. Mater. **20**, 506 (2008).
[4] Kreft, O., Skirtach, A. G., Sukhorukov, G. B., Möhwald, H.: Remote Control of Bioreactions in Multicompartment Capsules. Adv. Mater. **19**, 3142 (2007).
[5] Skirtach, A. G., Dejugnat, C., Braun, D., Susha, A. S., Rogach, A. L., Sukhorukov, G. B.: Nanoparticles Distribution Control by Polymers: Aggregates versus Nonaggregates. J. Phys. Chem. C **111**, 555 (2007).

Active Interfaces and Coatings

Dmitry Shchukin 11.11.1976

1998: Diploma
Electrochemistry of Conductive
Polyaniline Films (Belarusian State
University, Minsk, Belarus)

2002: PhD, Binary TiO_2-based
Photocatalysts (Belarusian State
University, Minsk, Belarus)

2002: Postdoc,
(Max-Planck Institute of Colloids
and Interfaces, Potsdam)

2003: Postdoc,
(Louisiana Tech University, Ruston, USA)

2004: Alexander von Humboldt Fellow,
(Max-Planck Institute of Colloids
and Interfaces, Potsdam)

2005/2006: Incoming Marie Curie Fellow,
(Max-Planck Institute of Colloids
and Interfaces, Potsdam)

Since 2006: Group leader,
Department of Interfaces,
(Max-Planck Institute of Colloids
and Interfaces, Potsdam)

References:

[1] Shchukin, D.G., Möhwald, H.:
Surface Engineered Nanocontainers for
Entrapment of Corrosion Inhibitors, Adv.
Funct. Mater., **17**, 1451-1458 (2007).

[2] Skorb, E.V., Antonouskaja, L.I.,
Belyasova, N.A., Shchukin, D.G., Möh-
wald, H., Sviridov, D.V.: Antibacterial
Activity of Thing-Film Photocatalyst
Based on Metal-Modified TiO_2 and
TiO_2:In_2O_3 Nanocomposite, Appl. Catal.
B: Environmental, **84**, 94-99 (2008).

[3] Andreeva, A.V., Shchukin, D.G.:
Protective Coatings with Smart Self-
Repairing activity, Materials Today, **11**,
24-30 (2008).

[4] Shchukin, D.G., Lamaka, S.V.,
Yasakau, K.A., Zheludkevich, M.L., Fer-
eira, M.G.S., Möhwald, H.: Active Anti-
corrosion Coatings with Halloysite
Nanocontainers, J. Phys. Chem. C, **112**,
958-964 (2008).

[5] Grigoriev, D.O., Bukreeva, V., Möh-
wald, H., Shchukin, D.G.: New Method

General development of multifunctional coatings, which will possess active and rapid feedback activity in response to changes in local environment, is a key technology for fabrication of future high-tech products and functional surfaces **[1-11]**. These new multifunctional coatings should combine passive components of "classical" coatings and active components, which provide fast response of the coating properties to changes occurring either in the passive matrix of multifunctional coatings (e.g., cracks, local pH change) or in the local environment surrounding the coating (electromagnetic irradiation). The coatings could also have several functionalities.

Nanocontainers

The release properties and re-loading ability of polyelectrolyte-modified halloysite nanotubes, SiO_2 nanoparticles, and polyelectrolyte capsules were studied **[1, 4, 6]**. All nanocontainers revealed an increase of the inhibitor (benzotriazole) release in aqueous solution at alkaline or acidic pH. The application of appropriate nanocontainers depends on the demands required from feedback active anticorrosion coatings. For coatings where the immediate release of the inhibitor is necessary, SiO_2-based or halloysite-based nanocontainers with the shell made of weak polyelectrolytes are preferable. When continuous, gradual release is required, halloysite-based nanocontainers with shell made of one weak polyelectrolyte and one strong or two strong polyelectrolytes are more favourable.

Protective Coatings

Sol-gel films provide excellent adhesion to the substrate and a suitable protection against corrosion by creating a chemically inert barrier between the substrate and the aggressive environment. However, these coatings cannot offer an adequate protection over long term due to the presence of micropores, cracks and areas with low cross-link density. In order to limit the corrosion process, surface modified mesoporous SiO_2 containers loaded with corrosion inhibitor (2-(benzothiazol-2-ylsulfanyl)-succinic acid) were incorporated into the sol-gel films **[2]**. The sol-gel film with containers, which act as a reservoir of corrosion inhibitor, diffuses through the container in aggressive medium and limits the corrosion process.

Halloysite aluminosilicate nanotubes with 15 nm lumen, 50 nm external diameter, and length of 800 ± 300 nm were developed as a container for loading, storage, and controlled release of anticorrosion agents and biocides **[4, 10]**. A fundamental research on nanoassembly to control the release rate within hours, days and months through varying internal fluidic properties and formation of nanoshells in the tube ends is in progress. Sustained activity, food additions, fertilizers, and drug sustained release, plastic fillers, radio wave adsorbing coating with metalized halloysite, and specific ion adsorbent are also in the list of possible halloysite applications. Halloysite nanotubes are available in thousands of tons, and remain sophisticated and novel natural nanomaterials.

Fig. 1: Long term corrosion test: aluminium alloy covered by the polyelectrolyte/inhibitor coating (left) and unmodified aluminium plate (right).

Multicomponent coatings formed by polyelectrolyte multilayers demonstrate a novel method of corrosion protection based on formation and deposition of polyelectrolyte multilayers on aluminium alloy surfaces **[3, 8, 9]**. The multilayer nanonetwork exhibits very high corrosion protection due to the nature and versatility of the polyelectrolyte complex. **Fig. 1** shows pictures of samples coated by the polymer/inhibitor complex (left) and without coating (right). Corrosion defects can be observed after 12 hours of immersion in 0.1 M NaCl on the unmodified aluminum whereas the sample with the polymer/inhibitor complex does not exhibit any visible signs of corrosion attack even after 21 days of immersion. The anticorrosion activity of the polyelectrolyte coating is based on the following mechanisms: 1) pH buffer formed by polybase and polyacid complex suppresses pH changes caused by corrosion degradation; 2) coating regeneration and defect elimination due to relative mobility of polymer chains in swollen state; 3) polyelectrolyte layers form a carrier for the inhibitor allowing its release on demand; 4) polyelectrolyte nanonetwork provides a barrier between surface and environment.

Sonochemistry with Nanoparticles

The collapse of the critical cavitation microbubble in liquids under ultrasonic treatment results in an enormous concentration of energy from the conversion of the surface energy and kinetic energy of the liquid motion into heat or chemical energy. The high local temperatures (5000-7000 K inside a cavitation bubble) and pressures combined with rapid cooling provide unique means for forming nanomaterials with non-equilibrium structure under extreme conditions **[12-19]**. The characteristics of the ultrasonically produced nanomaterials can be changed by decorating it with suitable hydrophilic and hydrophobic organic moieties.

Sonication of silicon or other water-immiscible oils in a protein or polymer aqueous solution results in the formation of protein containers which have a polymer shell and an oil core [13, 15, 17, 19]. Small containers with size less than 3 µm are automatically sedimented after 3 months aging due to the high density of the shells while big containers tend to float on top of the dispersion. To further functionalize the container, magnetic or other nanoparticles can be deposited
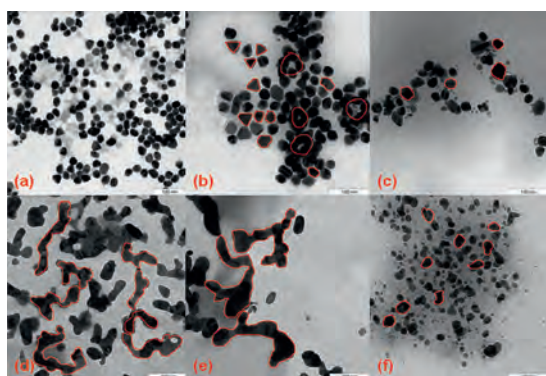

Fig. 2: Transmission electron microscopy images of (a) the control gold nanoparticles; (b) gold-silver nanostructures formed after sonication in aqueous solutions of silver nitrate and sodium borohydride; (c) gold-silver sonication of gold nanoparticles in silver nitrate and poly vinyl pyrrolidone in ethylene, (d) gold-silver after sonication in the presence of silver nitrate and sodium dodecyl sulphate in propanol and (e) in water; (f) gold-silver composites after sonication in the presence of silver nitrate and polyethylene glycol.

on the surface of the prepared containers by using the layer by layer technique. The loading of a dye in the containers shows the feasibility and simplicity used as carrier system. The loaded dye is stably kept inside and safely delivered for several weeks. The size of the containers is influenced by the power distribution in the ultrasonic vessel. An uneven power distribution in the ultrasonic vessel results in a broad size distribution of the prepared microspheres.

Stable monodisperse gold nanoparticles with the average diameter of 30 nm were used for modification by ultrasound at room temperature. The prepared gold nanoparticles were mixed with silver salt and successively sonicated step by step [12]. The successive ultrasonic treatment was found as the optimal one because it helps to avoid undesirable aggregation of gold nanoparticles and partly reduces silver ions during the sonication. The type of surfactant influences the size and shape of gold-silver alloys as well as the duration of the ultrasonic treatment adjusts the complete reduction of silver ions on the gold surface. Only 10 minutes of sonication are enough to form monodisperse polygonal gold-silver structures and less than 1 hour for their production with PVP in ethylene glycol solution (Fig. 2). More than 1 hour of ultrasonic irradiation is required to create gold-silver worms or net-like gold-silver nanostructures capped in between with SDS either in water or propanol. This effect was noticed for worm or net-like gold-silver nanocomposites

in the presence of SDS either in propanol or in water. XRD and ED patterns of final samples proved the presence of polycrystalline or amorphous gold-silver nanoalloys.

The similar effect of ultrasonic treatment on the crystallinity and activity of platinum nanoparticles was also observed [14]. Amorphous platinum nanostructures were formed after 20 min of sonication in water, whereas in poly vinyl pyrrolidone or ethylene glycol solutions they became crystalline. The fastest catalysis was driven by platinum nanoparticles after sonication in ethylene glycol solution for 20 min, while the lowest one was found for those after the ultrasonic treatment for one hour in poly vinyl pyrrolidone aqueous solution.

Multilayered Na$^+$-montmorillonite clays intercalated with Au nanoparticles were synthesized by direct ultrasonic impregnation of pre-formed gold colloid into the clay matrix. The sonicated composite product consists of Au nanoparticles homogeneously dispersed in the clay. The sample loaded from 4.2 % wt. colloid solution provides the saturation level for Au impregnation into clay material. The nanocomposites are thermally stable as was shown by thermogravimetric analysis. No aggregation of the gold nanoparticles was observed during calcination.

D. Shchukin, D. Andreeva, V. Belova, T. Borodina, D. Fix, D. Grigoriev, M. Haase, Y.-S. Han, I. Dönch, B. Parakhonskiy, R. Pflieger, A. Praast, D. Radziuk, G. Toquer, K. Skorb, J. Schneider, H.-M. Xiong,
dmitry.shchukin@mpikg.mpg.de

for Fabrication of Micro- and Nanocontainers: Emulsion Encapsulation by Polyelectrolyte Layer-by-Layer Deposition on the Liquid Core, Langmuir, **24**, 999-1004 (2008).

[6] Shchukin, D.G., Möhwald, H.: Self-Repairing Coatings Containing Active Nanoreservoirs, SMALL, **3**, 926-943 (2007).

[7] Grigoriev, D.O., Möhwald, H., Shchukin, D.G.: Theoretical Evaluation of Nano- and Microparticulate Contact Angle at Fluid/Fluid Interfaces: Analysis of the Excluded Area Behavior upon Compression, Phys. Chem. Chem. Phys., **10**, 1975-1982 (2008).

[8] Andreeva, D.V., Fix, D., Möhwald, H., Shchukin, D.G.: Buffering Polyelectrolyte Multilayers for Active Corrosion Protection, J. Mater. Chem., **18**, 1738-1740 (2008).

[9] Andreeva, D.V., Fix, D., Möhwald, H., Shchukin, D.G.: Self-Healing Anticorrosion Coatings Based on pH-sensitive Polyelectrolyte/Inhibitor Sandwich-Like Nanostructures, Adv. Mater., **20**, 2789-2794 (2008).

[10] Lvov, Y.M., Shchukin, D.G., Möhwald, H., Price, R.R.: Halloysite Clay Nanotubes for Controlled Release of Protective Agents, ACS Nano, **2**, 814-820 (2008).

[11] Lamaka, S.V., Shchukin, D.G., Andreeva, D.V., Zheludkevich, M.L., Möhwald, H., Ferreira, M.G.S.: Sol-Gel/Polyelectrolyte Active Corrosion Protection System, Adv. Funct. Mater., **18**, 3137-3147 (2008).

[12] Radziuk, D., Shchukin, D.G., Möhwald, H.: Sonochemical Design of Engineered Gold-Silver Nanoparticles, J. Phys. Chem. C, **112**, 2462-2468 (2008).

[13] Han, Y., Radziuk, D., Shchukin, D.G., Möhwald, H.: Stability and Size Dependence of Protein Microspheres Prepared by Ultrasonication, J. Mater. Chem., **18**, 5162-5166 (2008).

[14] Radziuk, D., Möhwald, H., Shchukin, D.G.: Ultrasonic Activation of Pt Catalyst, J. Phys. Chem. C, **112**, 19257-19262 (2008).

[15] Han, Y., Radziuk, D., Shchukin, D.G., Möhwald, H.: Sonochemical Synthesis of Magnetic Protein Container for Targeted Delivery, Macromol. Rapid Commun., **29**, 1203-1207 (2008).

Ordering of Functional Nanoparticles

Dayang Wang 29.04.1972
1993: B. Eng. Chemistry,
(Jilin University, China)
Thesis: Synthesis and characterization
of side-chain liquid crystalline
poly(6-[4-(p-nitrophenyl)azo]phenoxy-1-
hexyloxy maleic acid monoester).
1998: PhD, Chemistry
(Jilin University, China)
Thesis: Polymer-directed synthesis of
inorganic nanoparticles for high density
information processing and storage.
1999: Postdoctoral Fellow
(Dept. Mech. Eng., Hong Kong
University of Science and Technology,
Hong Kong)
2000-2003: Postdoctoral Fellow
(Max Planck Institute of Colloids
and Interfaces, Potsdam)
2001: Alexander von Humboldt research
Fellow (Max Planck Institute of Colloids
and Interfaces, Potsdam)
Since 2003: Group leader
(Max Planck Institute of Colloids
and Interfaces, Potsdam)

Due to the unique dimension and the size-dependent physicochemical properties derived thereof, organization of colloidal nanoparticles (NPs) not only leads to advanced materials, but also provides experimental accessibility to understand the packing symmetry and the interaction balance of elemental particles. Up to date, however, our capability to instruct colloidal NPs to self-assemble into tailor-designed structures is limited. To overcome this limit, one should re-visit the thermodynamics associated with self-assembly of colloidal NPs, such as the acting nature of various forces exerted on the NPs and the balance between the forces. In parallel, one should also enhance the capability to synthesize colloidal NPs with anisotropic morphologies and/or patterned surface functionality. To achieve a better control of the spatial configurations of the self-assemblies of colloidal NPs and even a flexibility to tune their spatial configurations by using external fields or stimuli, new flexible templates are also highly demanded such as the interfaces between two immiscible fluids and molecular self-assemblies. Only after accomplishing the above three tasks, one will be able to direct self-assembly of colloidal NPs in a spatially and temporally programmed fashion, leading to Supraparticles with the structural and functional complexity embodied in supramolecules [1].
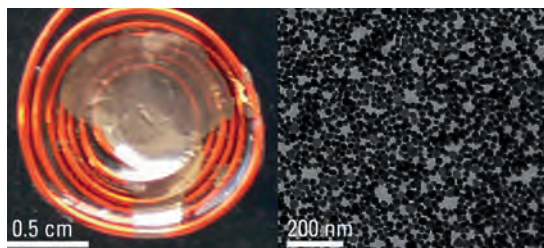
A. Interfacial Behavior of Nanoparticles

Fig. 1: Optical photograph (left) and transmission electron micrograph (right) of the dried freestanding monolayer film of 12 nm gold NPs, obtained by their self-assembly at the water/pentanol interface in a Petri dish, followed by heating at 48°C for 3 h.

The interfaces between two different phases allow molecules and macromolecules to accumulate and cross, which are of essential importance in everyday processes from biology such as transmembrane diffusion to geology such as oil extraction. Despite of a long research history in colloid science, the interface has just recently been appreciated by other research disciplines; the fluidic character allows formation of the NP monolayer films over large areas (at least several cm²). Taking the advantage of the exceedingly high surface energy of bare NPs, we succeeded in using water/oil interfaces to create dried freestanding monolayer films of metallic NPs, such as gold, silver, and platinum, with thickness ranging from 5 to 25 nm. **(Fig. 1) [2]**. It is of interest that the resulting freestanding films showed a certain mechanical robustness; the Young's modulus of dried freestanding films of 12 nm gold NP monolayers was determined as 1.6 GPa.
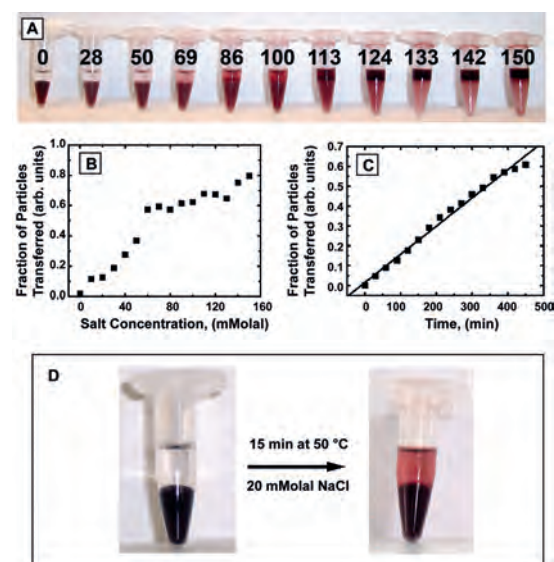

Fig.2: Poly (OEGMA-co-MEO₂MA) capped gold NPs spontaneously transfer across the salty water-toluene interface.

A) Optical image of poly (OEGMA-co-MEO₂MA) capped gold NPs originally dispersed in aqueous NaCl solutions, two days after creating a biphasic system with toluene. The NaCl concentrations, in mM, are shown on each vial.

B) The fraction of Poly (MEO₂MA) capped gold NPs transferred across the salty water-toluene interface after 1 h as a function of salt concentration.

C) The fraction of poly (MEO₂MA) capped gold NPs transferred across the salty water (150 mM NaCl) - toluene interface as a function of time.

D)Optical image of Poly (OEGMA-co-MEO₂MA) capped gold NPs originally dispersed in a 30 mM NaCl solution in water 15 min after the introduction of toluene at room temperature and 15 min after heating the biphasic mixture at 40°C.

In order to use the interface well to template self-assembly of colloidal NPs, our research focus was also laid on mimicking the interfacial behavior of molecules. With the aid of atom transfer radical polymerization, we synthesized various polymers with one end terminated with different functional groups such as disulfide, carboxylic acid and catechol groups to be grafted on different NPs. When NPs were coated with stimuli-responsive polymer brushes, their surface energy, mainly hydrophobicity here, were able to be tuned in response to the environmental stimuli such as ionic strength and temperature. The stimuli-responsive hydrophilic-hydrophobic transition allowed NP transfer between the aqueous and organic phase across the interface when they were brought into a water/oil biphasic system **(Fig. 2) [3]**. As well known, colloidal NPs quickly attach to the interface, which should block the NP transfer across the interface. Accordingly, this new trans-interfacial behavior of NPs is size-dependent.

B. Directed Self-Assembly of Nanoparticles

One of our major research activities associated with directing self-assembly of colloidal NPs is to understand the nature of various forces exerted on NPs during the self-assembly and
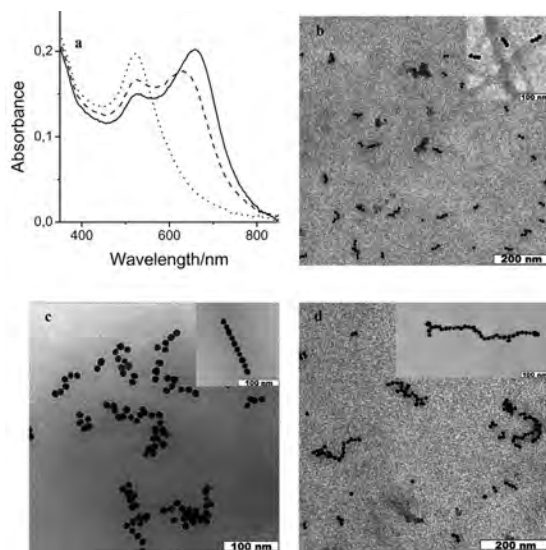
Fig. 3: (a) UV-vis spectral evolution of gold NP dispersions as a function of the water-to-acetonitrile volume ratio, 1:1 (dotted curve), 1:2 (dashed curve), and 1:3 (solid curve). TEM images of chains of gold NPs obtained using water-to-acetonitrile volume ratios, 1:1 (b), 1:2 (c), and 1:3 (d). The corresponding high magnification TEM images are shown in the insets.

how to control the thermodynamic balance of the forces between the NPs. It is well recognized that charged NPs are not stable and tend to aggregate upon adding salt into their dispersions due to the dramatic reduction of the electrostatic repulsion. After capping negatively charged gold NPs with thiol-ligands to enhance the dipolar interactions arising from the uneven surface morphology and non-uniform surface

crystalline facets by Au-S bonding, we recently found that the gold NPs commenced to chain up and the chain growth could be tuned exclusively by the electrostatic repulsion between the NPs **(Fig. 3) [4]**. Lowering the electrostatic repulsion between the gold NP led to longer the NP chains. As compared with the ionic strength of the surrounding media, the dielectric constant provided a better tool to tune the electrostatic repulsion between the charged gold NPs. Our study suggests that although the long-range electrostatic repulsion between charged particles is isotropic in nature, it can act in an anisotropic way in the presence of short-range anisotropic interactions such as dipolar interaction, thus endorsing an anisotropic agglomeration of NPs. This allows us not only to direct self-assembly of colloidal NPs in a controlled one dimensional way but to gain a better understanding of nucleation and agglomeration of charged species in aqueous media where electrostatic forces are not negligible.

C. Colloidal Lithography

Self-assembly of colloidal NPs should be integrated with macroscopic and microscopic devices in order to make a great impact on our society. The patterning techniques used to construct devices are mainly based on lithography, which are little accessible to chemists, biologists and materials scientists. Accordingly, in the past years our journey of using single and double layers of hexagonally closely-packed colloidal microsphere continued to pursue a cheap, flexible, and nanochemcial way to create patterns with feature complexity comparable to those obtained by lithography. Recently, we have successfully developed a stepwise angle-resolved colloidal lithography with the aid of plasma etching of the colloidal template.
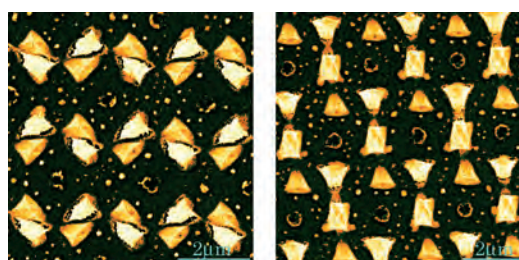
Fig.4: Heterogeneous binary arrays of gold (yellow) and silver (white) NPs obtained by stepwise angle resolved colloidal lithography.

With the new technique, we were able to create 2D and even quasi-3D patterns on planar substrates with defined but varied lateral and vertical heterogeneity, some of which are hard to create even by lithography **(Fig. 4) [5]**.

D. Wang, H.-J. Ahn, S. Bai, M. Chanana, Z. Chen, D. Kohler, W. Li, H. Liu, M. Meckelburg, Y. Nie, H. Xia, H. Xu, H.-K. Yu and B. Zhang,
dayang.wang@mpikg-golm.mpg.de

References:

[1] Edwards, E., Wang, D. Möhwald, H.: Hierarchical Organization of Colloidal Particles: From Colloidal Crystallization to Supraparticle Chemistry, Macromol. Chem. Phys. **208**, 439-445 (2007).

[2] Xia, H., Wang, D.: Fabrication of Freestanding Films of Metallic Nanoparticle Monolayers via Interfacial Self-Assembly Adv. Mater. **20**, 4253-4256 (2008).

[3] Edwards, E. W., Chanana, M., Wang, D., Möhwald, H.: Stimuli-Responsive Reversible Transport of Nanoparticles across Water-Oil Interfaces, Angew. Chem. Int. Ed. **47**, 320-323 (2008).

[4] Zhang, H., Wang, D.: Controlling Chain Growth of Charged Nanoparticles Using Interparticle Electrostatic Repulsion Angew. Chem. Int. Ed. **47**, 3984-3987 (2008).

[5] Zhang, G., Wang, D.: Fabrication of Heterogeneous Binary Arrays of Nanoparticles via Colloidal Lithography, J. Am. Chem. Soc. **130**, 5616-5617 (2008).

Molecular Assemblies of Biomimetic Systems and Nanostructured Design

Junbai Li 01.12.1964
1989: Diploma, Chemistry
(Jilin University, China) Thesis: Photon
Correlation Spectroscopy Investigation
of Ultrafine Polymer Particles
1992: PhD, Chemistry
(Jilin University, Mainz University)
Thesis: Homodyne Correlation Spectro-
scopy of Macromolecular Ultrafine
Particle in Solution and Dynamic
Light Scattering of Thermally Excited
Capillary Waves on a Liquid Surface
1993: Postdoc
(Foundation of Research
and Technology, Hellas)
1994-1996: Postdoc
(Max Planck Institute of Colloids
and Interfaces, Potsdam)
1996: Full Professor
(International Joint Lab, Institute
of Photographic Chemistry,
Chinese Academy of Sciences)
Since 1999: Full Professor
(International Joint Lab,
Institute of Chemistry, Chinese
Academy of Sciences)

Biomimetics has proved very useful in the design and fabrication of new functionally structured materials on the micro- and nanoscale. Biomimetics refers to human-made processes, devices, or systems that mimic or imitate certain aspects of biological systems, which has proven useful in providing biological inspiration from natural efficient designs. However, biomimetic is not limited to just copying nature because, with the development of modern biology, scientists can directly utilize biological units themselves to construct hybrid nanostructured materials. Thus, some of the manufacturing difficulties of biomimetics can be avoided. Accordingly, the objective of our group is to integrate natural molecular machines such as motor proteins into the engineering of active biomimetic systems so that new functional hybrid nanomaterials can be constructed.

A. Active Biomimetic Systems
Regeneration of ATP Biosynthesis in Assembled Capsules

The F_0F_1-ATPase is responsible for the catalytic synthesis of ATP molecules in biological organisms. They are widely present in the membranes of mitochondria, chloroplasts and prokaryotic cells, where they convert transmembrane electrochemical proton gradients into ADP~P bonds (i.e. ATP). The F_0F_1-ATPase is a well-known rotary motor and probably the best-understood biological molecular motor. ATPase assembled in lipid-modified polyelectrolyte micro-capsules is able to perform the process of ATP biosynthesis and provides a novel routine to fabricate bionanodevices. This assembled complex can not only help us to understand the biological function of ATPase molecules but also to construct such an artificial designed system containing ATPase providing a well-defined container for the storage of the energy currency ATP. When vital activities need energy, ATP will be released across the wall of the capsules as power supply **(Fig. 1)**.
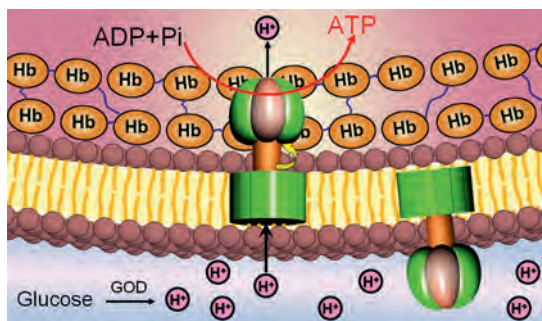

Fig. 1: Schematic representation of the arrangement of CF_0F_1-ATPase in lipid-coated microcapsules.

Assembled Capsule Transportation Driven by Motor Proteins

The linear molecular motor, kinesin, transports chemical pay-loads along microtubules in the cell. The used filament, microtubule, is polar and has two functions: provide rails or tracks for the kinesin motors and limit the movement in a certain direction. Our group currently focuses on the design and assembly of active biomimetic systems which involve the surface modification of microcapsules with well defined properties, purification of microtubules to link the bio-molecular motors, stepping motor proteins, kinesin and the completed assembly of the system. We try to provide experimental evidence on the way the molecular motors generate pulling forces to direct the hollow capsule transportation along the microtubules and further understand the force generation mechanisms. The final system aims at a specific function of hollow capsules as a useful "cargo" for drug delivery in a living matrix by making use of molecular motors **(Fig. 2)**.
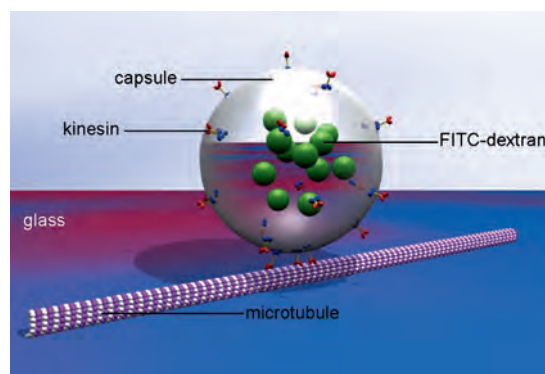

Fig. 2: Layer-by-layer assembled microcapsule as cargo driven by kinesins along a microtubule.

B. Bioinspired Nanostructures
Peptide Self-Assembly

Cationic dipeptides can self-assemble into the structure of vesicles spontaneously under a certain condition. Such a conversion could readily transport genes, into cells through the membrane. Interestingly, these cationic dipeptides can self-assemble into various types of fibrils, strands and tapes in organic solvents via weak intermolecular interactions. The self-assembly behavior of dipeptide nanostructures, can be exploited as a new class of molecular transporter for the delivery of a wide range of foreign substances such as drugs and proteins. Currently, we are interested in investigating the conversion process quantitatively and building up models. We also report that a single dipeptide molecule, which is probably one of the smallest peptide gelators, can self-assemble into persistent length nanofibrils in organic solvents and intertwist further to form gels. Such gels can be readily used to encapsulate quantum dots and gold nanoparticles through gelating the organic solution of nanocrystals. These organic-inorganic complexes can find their applications as optical and electronic materials and devices **(Fig. 3)**.
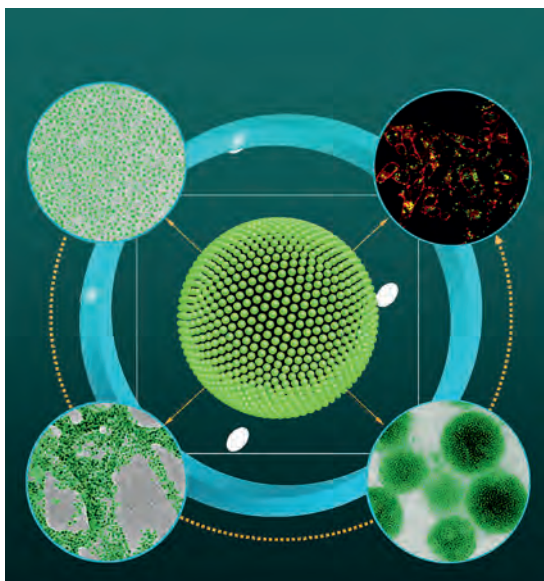
Fig. 3: Biocompatible water-dispersible 3D colloidal spheres can be prepared via the combination of functional lipophilic nanocrystals and a self-assembling cationic dipeptide building block.

Biointerfacing Multilayer Nanostructures

Polyelectrolyte multilayer-supported liposomes or lipid bilayer-coated polyelectrolyte multilayer nanostructures could be fabricated through the conversion of liposomes into lipid bilayers to cover the multilayers' surface in analogy to the cell membrane. These lipid-modified polymer microcapsules should be an ideally supported biomimetic membrane system to mimic a real cell membrane. Polyelectrolyte multilayer-supported lipid bilayer systems should be useful for the understanding of the principles of the interaction of membranes with biopolymers such as proteins, opening the possibility for the design and application of new biomimetic structured materials **(Fig. 4)**.
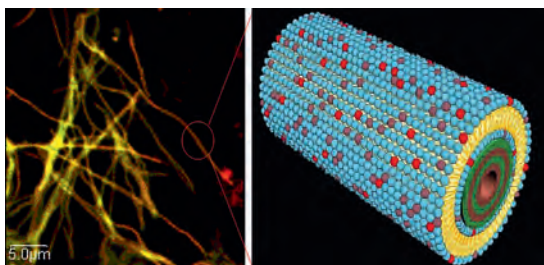

Fig. 4: Schematics of lipid bilayer coating on layer-by-layer assembled luminescent nanotube by liposome fusion.

Biomimetic Capsule as Photosensitive Drug

Photodynamic therapy (PDT) is a rapidly growing methodology to treat cancers, viruses and some special vascular diseases that are accessible to irradiation by visible light. Although light-sensitive drugs or photosensitizers can be activated by light, they should not interact directly with cells and tissue. Light-activated PDT drugs can generate singlet oxygen ($^1O_2$) which is a cytotoxic species to induce cell death. Obviously, this method has good selectivity because the cytotoxic reactions only occur in those tissues exposed to the photosensitizer and light. Hypocrellins and natural perylenequinoid pigments are thought of as potential photosensitizes in PDT.

Hypocrellin B (HB) has a wide absorption band in the visible region and extremely high singlet oxygen ($^1O_2$) generation ability and thus has been receiving intensive interest in PDT. However, HB is insoluble in water which limits its application in clinical treatments. We therefore introduce assembled hollow shells loaded with HB into PDT to overcome the obstacles of hydrophobicity of HB. These hollow shells are meant to deliver drugs into cell compartments and to allow the direct visualization of intracellular drug distribution **(Fig. 5)**.
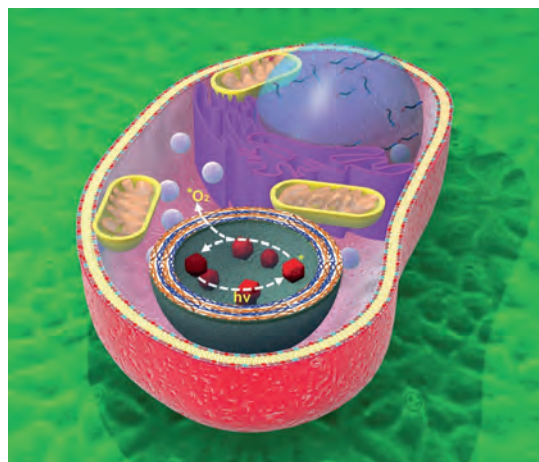

Fig. 5: Photosensitive drugs encapsulated by biomimetic microcapsules to incapacitate cancer cells.

J.B. Li, Q. He, Y. Cui, W.X. Song, D.X. Li, X.H. Yan, S.F. Ai, Y. Su, L. Duan.
Junbai.Li@mpikg.mpg.de

References:

[1] Qi, W., Li, D.X., Wang, K.W., Yan, K.W., Cui, Y., He, Q., Li, J.B.: ATP synthesis catalyzed by motor protein CF_0F_1 reconstituted in lipid-coated hemoglobin microcapsules. Adv. Mater. **20**, 601-605 (2008).

[2] Fei, J.B., Cui, Y., Yan, X.H., Qi, W., Yang, Y., Wang, K.W., Li, J.B.: Controlled preparation of MnO_2 hierarchical hollow nanostructures and their application in water treatment. Adv. Mater. **20**, 452-456 (2008).

[3] Yan, X.H., Cui, Y., Wei, Qi, Su, Y., Yang, Y., He, Q., Li, J.B.: Self-assembly of peptide-based colloids containing lipophilic nanocrystals. Small **4**, 1687-1693 (2008).

[4] Yan, X.H., Cui, Y., He, Q., Wang, K.W., Li, J.B., Mu W.H., Wang, B.L., Ou-yang, Z.C.: Reversible transitions between peptide nanotubes and vesicle-Like structures including theoretical modeling studies. Chem. Eur. J. **14**, 5974-5980 (2008).

[5] He, Q., Song, W.X., Möhwald, H., Li, J.B.: Temperature-induced structural transformation of polyelectrolyte multilayers: tube to capsule. Langmuir **24**, 5508-5513 (2008).

[6] He, Q., Zhang, Y., Lu, G., Miller, R., Möhwald, H, Li, J.B.: Dynamic adsorption and characterization of phospholipid and mixed phospholipid/protein layers at liquid/liquid interfaces. Adv. Colloid Interface Sci. **140**, 67-76 (2008).

[7] Duan, L., He, Q., Wang, K.W., Yan, X.H., Cui, Y., Möhwald, H., Li, J.B.: ATP biosynthesis catalyzed by the F_0F_1-ATP synthase assembled in polymer microcapsules. Angew. Chem. Int. Ed. **46**, 6996-7000 (2007).

[8] Yang Y., He Q., Duan L., Cui Y. Li J.B.: Assembled Alginate/Chitosan Nanotubes for Biological Application. Biomaterials **28**, 3083-3090 (2007).

[9] Yan, X.H., He, Q., Wang, K.W., Duan, L., Li, J.B.: Transition of cationic dipeptide nanotubes into vesicles and oligonucleotide delivery. Angew. Chem. Int. Ed. **46**, 2431-2434 (2007).

[10] Li, D.X., He, Q., Wang, K.W., Cui, Y., Yan, X.H., Li, J.B.: Thermosensitive nanostructures comprising Gold nanoparticles grafted with block copolymers. Adv. Function. Mater. **17**, 3134-3140 (2007).

Supramolecular Materializations

Takashi Nakanishi 19.02.1974

1996: B. Eng. Chemistry
(Nagasaki University, Japan)
Thesis: Synthesis and characterization
of novel electrochemical active
diarylethene.

2000: PhD, Chemistry
(Nagasaki University, Japan)
Thesis: Design of functional organic
thin films using fullerenes.

2001: JSPS Postdoctoral Fellow,
(University of Houston, TX, USA)

2002: JSPS Postdoctoral Fellow,
(Oxford University, UK)

2004: Researcher,

2007: Senior Researcher,
(National Institute for Materials
Science, Tsukuba, Japan)

2007: Group Leader,
(Max Planck Institute of Colloids
and Interfaces, Potsdam)

2007: Researcher,
(PRESTO, Japan Science and
Technology Agency, Japan)

An important challenge in nanoscience is to fabricate dimension-controllable nano/microscopic organic architectures which exploit the advantageous intrinsic properties and the weak intermolecular forces of their molecular building blocks. Nano/microscopic structure formation from typical (hydrophilic/hydrophobic) amphiphiles such as surfactants and lipids is well matured, and the formation mechanism is well understood. Our interests of research are focused to supramolecular architectures in nano/microscopic and bulk scales from functional components whose structures are far from conventional amphiphiles, which have more possibilities to create versatile assembled architectures and functions. A delicate balance of the intermolecular interactions, such as van der Waals, π-π, hydrogen-bonding, leads to a wide variety of supramolecular morphology and this understanding of hierarchically assembled systems should inspire further studies for supramolecular chemistry, biomimetic structures, nanotechnology as well as their materializations.

The Supramolecular method utilized in our group is controlling the architecture and dimensionality of hierarchical fullerene superstructures by varying the nature of the solvent system. To achieve the hierarchical fullerene assemblies, we have synthesized a series of new type of amphiphilic (solvophilic) fullerene derivatives bearing long aliphatic chains, especially three hexadecyloxy chains (1), and explored them by using the two different intermolecular forces, π-π (C_{60}) and van der Waals (aliphatic chains) interactions [1, 2]. By varying the solvent system, the derivative self-organized into vesicles, fibers, cones, micro-spheres, maracas-like, windmill-like sheets, jellyfish-like, left-handed and right-handed spiral objects (Fig. 1). The finding suggests possible synthetic methodologies towards novel dimension-controllable carbon materials.
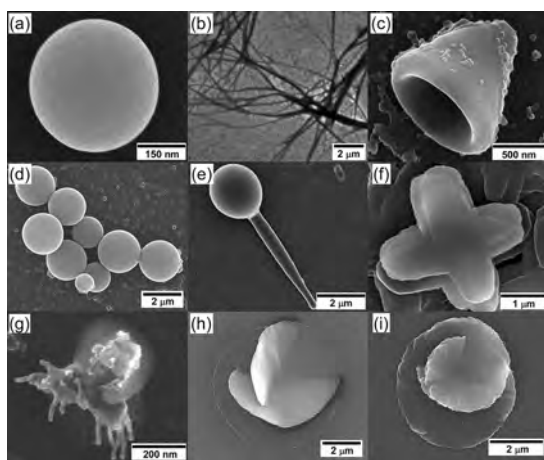
To further diversify the library of self-organized fullerene superstructures, for instance, with fractal shape, the understanding of the formation mechanism of self-organized microscopic superstructures becomes more important. Hierarchical supramolecular assemblies of micrometer-sized flower-shaped objects (Fig. 2) are constructed by transformation of an interdigitated bilayer precursor composed of a fullerene derivative (1). Intermediate transforming structures, which include flat bilayer disks, rolled up and crumpled disks, provide evidence for the formation mechanism of the flower-shaped objects [1].
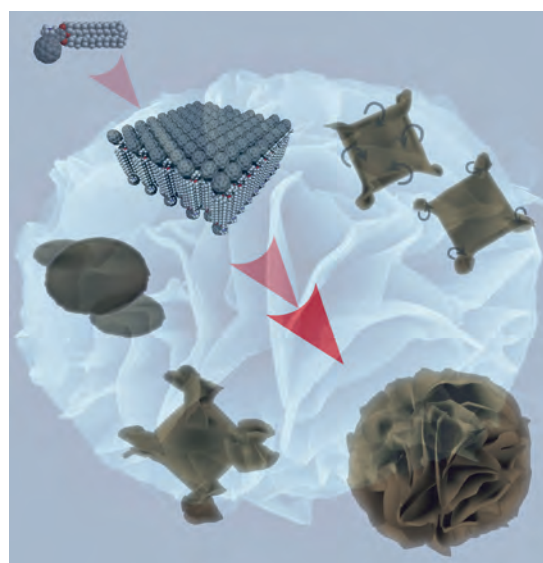

Fig. 2: Formation mechanism of flower-shaped supramolecular assemblies of 1.

A fullerene derivative bearing three eicosyloxy chains (2) self-assembled into micrometer-sized particles with wrinkled flake-like outer surface morphology. The assembled objects have more potential to be useful supramolecular materials due to their quantitative yields from the derivative, well-analyzed nano-assembled architectures (self-organized bilayer), and their ease of hierarchical fabrication on substrates. Thin films of these particles have a fractal surface reminiscent of the Lotus Leaf and feature water-repellent superhydrophobicity with a water contact angle of "152°" (Fig. 3) [3].
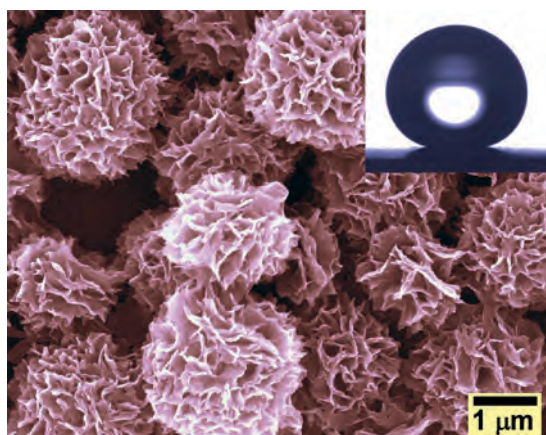

Fig. 1: SEM images of vesicles (a), fibrous (b), conical (c), microspherical (d), maracas-like (e), windmill-like sheets (f), jellyfish-like (g), left-handed (h) and right-handed (i) spiral objects of 1 obtained from various solvent conditions.

Fig. 3: SEM image of globular assemblies of 2 having nanoflaked outer surfaces. Inset shows a photograph of water droplet on the surface (contact angle of 152°).

A sustainable method for the fabrication of metallic surfaces with rose flower-like fractal morphology was developed by using the supramolecular microparticles of 2 as templates, which possess a nanoflake structure at the outer surface **(Fig. 4)**. Modifying Au nanoflakes with self-assembled thiol monolayers or polymers allows the surface wettability to be adjusted between superhydrophilic and superhydrophobic. Furthermore, Au nanoflakes present excellent substrates for surface-enhanced Raman spectroscopy. The enhancement factor is around 10^5 **[4]**.

Fig. 4: Schematic illustration for the fabrication of metal nanoflake surfaces via supramolecular assemblies of a fullerene derivative (2) as template objects.

The fullerene derivatives satisfy the requirements for high carrier mobility in the C_{60}-containing mesomorphic materials: a high C_{60} content up to 50% and a highly ordered mesophase. Thermotropic mesophase of 2 is seen in the temperature range between 62 to 193°C, and shows optical texture under a polarized optical microscope **(Fig. 5a)**, which exhibits birefringence and confirms the fluid nature. Higher-order peaks, up to (0 0 14), in the XRD pattern reveal a long-range ordered lamellar mesophase comparable to ordered smectic phases **(Fig. 5b)**. The mesomorphic fullerenes feature reversible redox activity and comparably high electron carrier mobility, ~3×10^{-3} cm^2/Vs at 120°C, making them attractive components for fullerene-based soft materials **[5]**.
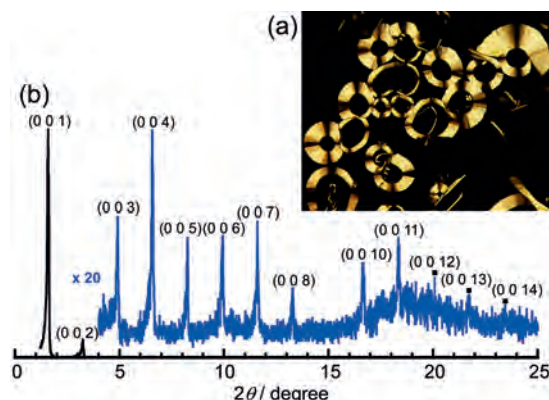

Fig. 5: Polarized optical micrographic texture (a) of mesophase of 2 at 190°C and the XRD patterns (b) indicating its long-range ordered lamellar organization.

Other areas of interest include supramolecular materials of dipyrrole-diketon type versatile assemblies **[6]**, anion sensible organogels **[7]** and diversification of barbituric acid merocyanine dye architectures by hydrogen-bonding **[8]**.

T. Nakanishi, Y. Shen, J. Wang
Collaborated with MPI: H. Möhwald, D. G. Kurth
takashi.nakanishi@mpikg.mpg.de

References:

[1] Nakanishi, T., Ariga, K., Michinobu, T., Yoshida, K., Takahashi, H., Teranishi, T., Möhwald, H. and Kurth, D. G.: Flower-Shaped Supramolecular Assemblies: Hierarchical Organization of a Fullerene Bearing Long Aliphatic Chains. Small **3**, 2019-2023 (2007). (Cover Picture)

[2] Nakanishi, T., Wang, J., Möhwald, H., Kurth, D. G., Michinobu, T., Takeuchi, M. and Ariga, K.: Supramolecular Shape Shifter: Polymorphs of Self-Organized Fullerene Assemblies. J. Nanosci. Nanotechnol. **9**, 550-556 (2009).

[3] Nakanishi, T., Michinobu, T., Yoshida, K., Shirahata, N., Ariga, K., Möhwald, H. and Kurth, D. G.: Nanocarbon Superhydrophobic Surfaces Created from Fullerene-Based Hierarchical Supramolecular Assemblies. Adv. Mater. **20**, 443-446 (2008).

[4] Shen, Y., Wang, J., Kuhlmann, U., Hildebrandt, P., Ariga, K., Möhwald, H., Kurth, D. G. and Nakanishi, T.: Supramolecular Templates for Nanoflake-Metal Surfaces. Chem. Eur. J. **15**, 2763-2767 (2009). (Cover Picture)

[5] Nakanishi, T., Shen, Y., Wang, J., Yagai, S., Funahashi, M., Kato, T., Fernandes, P., Möhwald, H. and Kurth, D. G.: Electron Transport and Electrochemistry of Mesomorphic Fullerenes with Long-Range Ordered Lamellae. J. Am. Chem. Soc. **130**, 9236-9237 (2008).

[6] Maeda, H., Kusunose, Y., Terasaki, M., Ito, Y., Fujimoto, C., Fujii, R. and Nakanishi, T.: Micro- and Nanometer-Scale Porous, Fibrous, and Sheet Architectures Constructed by Supramolecular Assemblies of Dipyrrolyldiketones. Chem. Asian J. **2**, 350-357 (2007). (Inside Cover Picture)

[7] Maeda, H., Haketa, Y. and Nakanishi, T.: Aryl-Substituted C3-Bridged Oligopyrroles as Anion Receptors for Formation of Supramolecular Organogels. J. Am. Chem. Soc. **129**, 13661-13674 (2007).

[8] Yagai, S., Kinoshita, T., Higashi, M., Kishikawa, K., Nakanishi, T., Karatsu, T. and Kitamura, A.: Diversification of Self-Organized Architectures in Supramolecular Dye Assemblies. J. Am. Chem. Soc. **129**, 13277-13287 (2007).