→ Independent Researchers
→ (Quasi) Planar Interfaces – Fluid Interfaces
→ Solid Interfaces
→ Non-Planar Interfaces

INTERFACES

Research in the Department of Interfaces

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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. Macromolecules like proteins and peptides may change their secondary and tertiary structure and thus their function at interfaces. Within the institute`s 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. The latter is also due to the fact that there has been a continuous development of methods over years. Part of these developments has been commercialized within four start-up companies.

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. This concerns reorganization of molecules, their diffusion as well as collective motion like flow under a surface pressure gradient.

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 has been organized within five groups which are largely independent from the director but interact with me in varying intensity. Some scientists are also under my direct supervision which has been in special necessary when the group leader had left or if there was a topic to be taken up independent of the immediate interest of a specific group.

II. Research Highlights

II. 1 Planar Interfaces

The specially advanced expertise and methodology to study Langmuir monolayers at the air/water interface has been made use of in many model studies of systems interesting for various type of applications, to name but a few:

- It was shown that the formation of beta sheets of specifically designed peptides is influenced by different cations (Cu, Zn) as well by the interface where they are located. In all cases studied interfacial forces dominated the ionic forces (cooperation Prof. B. Koksch, FU Berlin).
- New zwitterionic phospholipid membranes have been developed that appear most suitable for DNA transfection (coop. Prof. Dobner, Univ. Halle). This cooperation has now been extended by a company interested in RNA delivery.
- As most exciting new direction I consider studies of monolayers of lipids with designed carbohydrate head groups synthesized in the group of V. da Silva in the department of Biomolecular Systems. *C. Stefaniu* in the Brezesinski group by grazing incidence X-Ray diffraction observed a crystalline lattice of the carbohydrates in addition to the one of hydrocarbon chains. In cooperation with *M. Santer* from the Theory department the structure that is determined by hydrogen bonds could be solved. This opens new ways of cooperation between 3 departments where the molecular recognition of this attractive class of molecules can be studied with atomic resolution, including the consequences for coupled enzymatic reactions at membrane surfaces (**Fig. 1**).

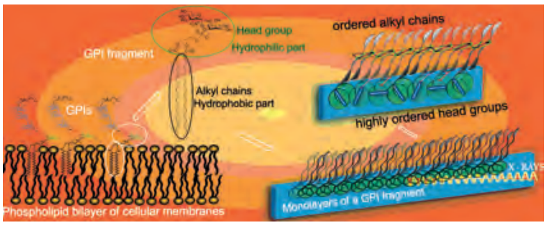

Fig.1

The group of *R. Miller* has been continuing their studies of thermodynamics and rheology of charged amphiphiles at water/air and water/oil interfaces. By systematic variation of the chain length they demonstrate that the adsorption isotherms can only be described by a Frumkin model that is extended by a term taking into account the Coulomb interactions of the head groups and the corresponding ion cloud. This model is also successful to describe surface rheology.

By systematically varying the chain length of alcanes and aliphatic oil they could show that the continuous film of detergent at the oil/ water interface incorporates the oil only if the oil has a specific chain length. This is understood as a compromise between van-der Waals forces and entropic forces that oppose the incorporation and orientation of the oil in the surfactant film (**Fig. 2**). The relevance of these studies for emulsion stabilization is reflected in various industrial co-operations of the group.

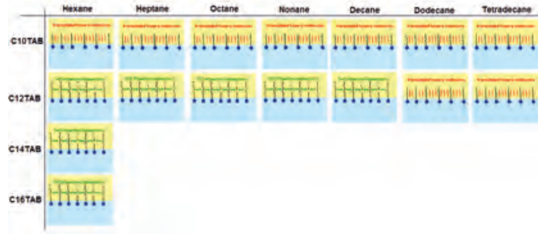

Fig.2

The group of *H. Riegler* has very much refined their optical and force microscopic observations of nucleation and growth of liquid bubbles on structured surfaces, thus yielding most quantitative data on interfacial interactions. They demonstrate that melting at steps on a surface may proceed by a nucleation and growth scenario which differs from that on flat surfaces or in bulk (coop. dept. Theory). In model studies of spin coating they calculate concentration profiles developing during the process and show that precipitates form at the liquid/air and liquid/solid interface. The latter can in addition be controlled by suitable surface structuring at the nm level. This is most relevant for a cooperation project with Helmholtz Center Berlin where nanosized aggregates of the phthalocyanines are used to fabricate bulk heterojunction solar cells.

They show that the contact angle of small droplets depends on their size and derive a model from which they obtain the line tension. They can quantitatively describe the size dependence of the contact angle by long range van der Waals forces assuming reasonable Hamaker constants.

They observe fast or delayed coalescence of sessile droplets of water/ oil mixtures. It depends little on viscosity but drastically on the surface tension difference. This indicates the importance of Marangoni flow and a corresponding model has been developed (coop. TU Cottbus). The quantitative description has been very much refined, and also the experiments have become most sophisticated by measuring the flow, controlling tightly environmental conditions (T, humidity) and numerically solving the corresponding hydrodynamic nonlinear equations (**Fig. 3**). Much of the work has been published in high impact journals, but it has also attracted industry funding, in special for wafer cleaning. (**Fig. 3**)

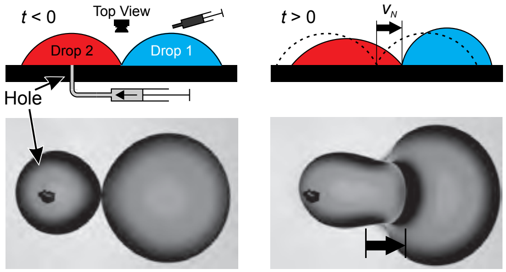

Fig.3

II. 2 Non-Planar Interfaces

The group of *D. Shchukin* has been engaged in basically two directions.

(A) Development of stimuli sensitive nanocontainers to be embedded in enabling the development of self-repairing coatings and studies of functions of self-repairing coatings.
(B) Development of sonochemistry as a tool for surface modification.

Under (A) nanotubular (halloysite) or nanoporous inorganic carriers were developed that via a polyelectrolyte multilayer shell exhibited stimuli sensitive release of incorporated corrosion inhibitors. Also polymeric capsules were developed via particle stabilized oil droplets (Pickering emulsions). After embedding in a coating they then could show that the different local pH near a defect can cause inhibitor release and thus annealing. It could be shown that size (between .5 and 5 mikrom.) and location of particles are most relevant for optimum corrosion protection. These studies are most promising for applications and will be pursued partly removed from the institute's main stream with the aim of developing a start-up company.

The activities under (B) were concentrated on determining the importance of surfaces to control cavitation. It was shown by microcontact printing that bubble nucleation in water can be confined to hydrophobic surface areas, and this will enable new ways of in-situ studies that are now in progress. Meanwhile it has been possible to quantify the cavitation density and to observe nanobubbles on a patterned surface by scanning force microscopy (**Fig. 4**) as well as by optical microscopy (V. Belova in coop. U. Göttingen).

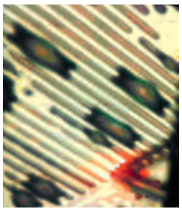

Fig. 4

The group of *A. Skirtach* has been most successful in making use of plasmonic interactions of metal nanoparticles and metal films. It has been made use of into three different directions:

- Following previous work on local heating by IR absorption Au nanoparticles were adsorbed to erythrocytes and cells to induce release of molecules from inside. This work has now become very elaborate to study the effect on certain channel proteins (coop. Charite and Jacobs Uni Bremen).

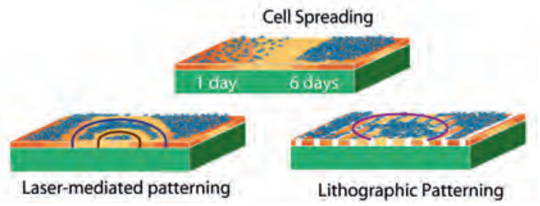

Fig.5:

- The high optical field enhancement near metal nanoparticles is well known. Adsorbing these particles into porous silica spheres one can achieve a high local density of these particles inside cells, and they are reachable by molecules inside the cell. This enables Raman detection and imaging of cellular components with light intensities close to sun light (coop. dept. Biomaterials).
- Via light induced melting patterns of nanoparticle distributions can be produced on a surface. As these change the surface mechanical properties also cell attachment follows this pattern. As alternative way singlet oxygen may be produced by light via the particles, and this in turn effects the growth and death of cells leading to cellular patterns (coop. University Bayreuth, dept. Biomaterials)

In the joint German-French lab on sonochemistry sonoluminescence spectra could be obtained from single bubbles existing of broad emission of a continuum from which a plasma temperature could be derived and the narrow emission from atomic or radical species, both depending drastically on the acoustic pressure. For rare earth ions it was shown that these ions were part of the plasma and not in the adjacent water phase .The work in this collaboration is now also extended towards composites of hydrogels in cooperation with the Biomaterials department.

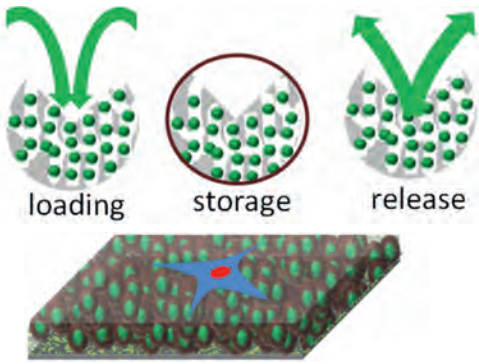

Fig. 6:

The work on cavitation has been successfully extended by 2 postdocs (V. Belova, Lu Zhang) to online measure cavitation and to quantify the influence of geometric surface features on cavitation. On the other hand cavitation has been extensively used to prepare porous surfaces (E.V. Skorb, **Fig. 6**) This offspring of the Shchukin group is now systematically extended to load the pores with drugs and to observe the response of cell attachment and growth (coop. Biomaterials).

As a most curiosity driven structure microtubes from designed peptides have been produced, and their structure resolved with molecular resolution (X.H. Yan). It was shown that these tubes can guide optical waves, but it will last for long till a physician will use the deposable light guide in an operation.

III. Future Development

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

- In 2011 *A.G. Skirtach* accepted a professorship in Biophotonics at University Gent. Members of the group are still working in the institute, engaged in many cooperations.
- In 2012 *D.G. Shchukin* accepted a call for a chair at University Liverpool. Also his group continued working on the many well-funded projects in the institute.
- *X.H. Yan* has received a professorship from the 1000 young talents program and just starts at the Institute of Process Engineering of the Chinese Academy of Sciences in Beijing.

Continuing collaboration with these groups it has been possible to maintain a size of about 50 people, hence to further shrink the department only in its last year of existence. Because of the strong external funding it has also been possible to finance this size in spite of the drastic reduction of the institutional funding.

As it has not yet been possible to continue with five departments, the interfaces department will be terminated with my retirement in January 2014. This means that the remaining groups have to be transferred into the existing departments at Golm. It is obvious from this report that the monolayer work of the Brezesinski already has many cooperations with all departments and also the Riegler group is well connected with theory, and so they may profit from this move.

The work on self-repairing coatings (Shchukin) has very much matured that it also withstood industrial tests. There are now intensive trials to transfer this knowledge and the people involved into a company. If this will be successful depends more on business and marketing issues not on technical ones. On the other hand the science concerning feedback-loops is often found in nature, e.g. to regulate pH, concentration of ions, enzymes, drugs, temperature or potential. Therefore it is not too surprising that it has carried *D. Shchukin* on a chair where he can broaden his research. The work on nanoplasmonics (Skirtach) has been profiting very much from in-house and external collaborations, and is expected to persist beyond my retirement above all in collaboration with the Biomaterials department. The latter collaboration will also be very promising with sonochemical surface treatment to control cellular interactions, and *E.V. Skorb* is expected to move there.

Major recognitions have been the award to *X.H. Yan* in the 1000 talents program and the election of *R. Miller* as president of the International Association of Colloids and Interfaces (IACIS). I have become member of the Academia Europaea.

As mentioned before the department of interfaces will persist another year, and it is a good tradition that a retiring director has no influence on the future direction and persons. It is also most desirable not to continue the “old” directions. Therefore I will not comment on any future perspectives of the department. On the other hand my colleagues are trying hard to maintain an institute with five departments and there is consensus that this should focus in a broad sense on physical chemistry. On the other hand I am satisfied that up to now the shrinking process has not encountered many personal hardships, as technicians, PhD students and postdocs found attractive positions. This was possible, because of the world wide connections of the department and of the institute as a whole.

Of course I would be disappointed if physical chemistry of interfaces disappeared from the institute, more importantly the Max Planck Society would not do wise to weaken an institute like ours this way. On the other hand I have no worry about the specific field. It encounters tremendous progress worldwide, and we have a considerable contribution to this. There are meanwhile more than 100 alumni from the department on professor positions or equivalent academic positions, and these will enhance science in the area. They all remember their time in the institute with pleasure and thanks, and therefore the time together has been worth it.

Helmuth Möhwald
Director of the Department of Interfaces

Peptide Optical Waveguiding

Biomimetic or bio-inspired functional materials with ordered organization at micro- or nanoscale, fabricated from peptide building blocks, are of increasing importance due to their potential application in biomedicine and nanotechnology. The self-assembled peptide superstructures with defined spatial dimensions hold great promise for creation of photonic or electronic materials. In this work, peptide optical waveguides were for the first time fabricated in the form of either solid platelets or hollow microtubes by confined assembly or crystallization of pathogenic amyloid fibrils. Peptide waveguides will naturally degrade and not leave any trace after they have acted as an optical element. Therefore, such functional structures of materials fabricated through self-assembly of versatile peptide molecules are advantageous in guiding light for biologically based modulation and sensing.

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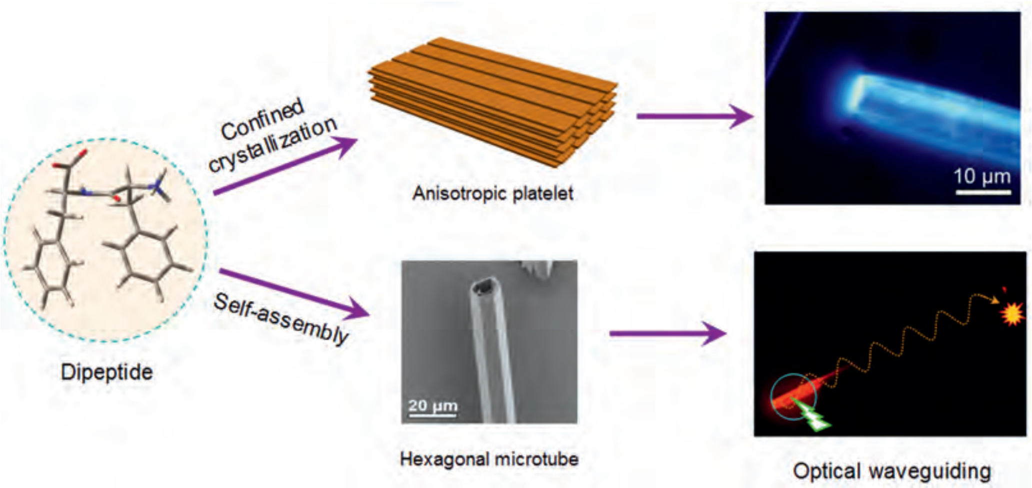

Fig. 1: Scheme and electron microscopic picture (middle bottom) of peptide assembly to platelets or tubes. The fluorescence micrograph right bottom shows at the lower left optical excitation of a microtube that is coupled out at the other end (small dot top right)

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[2] Yan, X.H., Li, J.B., Möhwald, H.: Self-assembly of hexagonal peptide microtubes and their optical waveguiding. Adv. Mater. **23**, 2796-2801 (2011).
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INDEPENDENT RESEARCHERS

Surface Nanoarchitecture for Self-Regulated Intelligent Interfaces

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The surface nanoarchitecture providing spatially and temporally resolved stimuli response of a material and offering defined control over the behaviour of biomolecules and cells at the solid-liquid interface is in focus in our reseach. In particular, in our recent works **[1-5]** we suggested effective ultrasonic assisted pathways of porous material formation (metals, silicon, hybrids and nanocomposites) which can find application for drug delivery vis-à-vis being used as capsules. In (**Fig. 1**) is shown the suggested strategy for formation of surface capsules. Thus after ultrasonic treatment of an aluminum surface a mesoporous layer with good adhesion to the bulk metal matrix is formed. The mesoporous surface layer can be loaded with a variety of agents (corrosion inhibitors, biocides, enzymes, DNA fragments, antibodies). Thus, the loaded metal layer has functionality of porous capsules. Comparing to existing encapsulation systems the surface capsules continue the bulk metal and don't need to be immobilized on the surface or incorporated into a protective coating. Furthermore, the rough surface of the metal capsules provides excellent adhesion of a protective coating.

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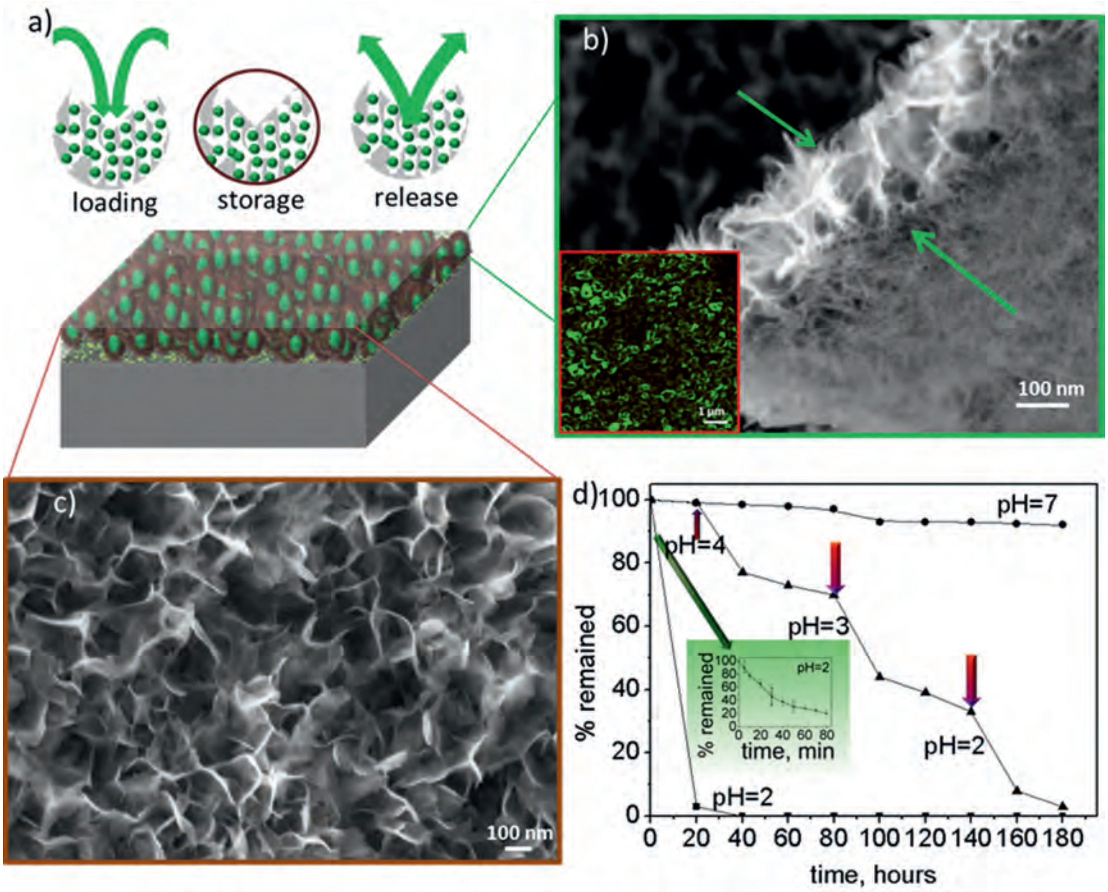

Fig. 1 (a) Schematic illustration of uploading, storage and release of active components (upper row) and general view of capsules generated at the metal surface (below). (b) SEM image of the cross section of an aluminum sponge-like layer (indicated by arrows). Luminescence confocal image (top view) of the surface capsules loaded with doxorubicin (inset). (c) TEM image of aluminum with a surface capsule layer for chemical storage (blue arrows show the loading direction, red arrows show the interface between bulk metal and capsules' layer). (d) Doxorubicin release at different pH and upon varying the pH as indicated by the red arrows. [4]

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Ultrasonic Cavitation on Particle Surfaces

Ultrasound has received significant attention in the development of new functional materials and composite nanostructures due to the distinctive effect of ultrasound on materials **[1-3]**. The understanding of ultrasonic cavitation on solid surfaces can greatly advance the application of ultrasound. Currently, studies have been mainly focused on the evolution of cavitation bubbles formed at planar surfaces **[1-4]**. Nevertheless, these results have not fully accounted for the geometry of the surfaces as they neglect the contribution of feature shapes. To improve the understanding of the cavitation process, SiO_2 particles of different sizes and shapes were irradiated under a series of ultrasonic parameters (**Fig. 1**). Through observing different surface changes of particles resulting from cavitation, a speculative mechanism of ultrasonic cavitation on particle surfaces was proposed. During bubble collapse, nano-sized particles will become rough and small by the high velocity collisions among particles while micron-sized particles can be broken due to the microjets and associated shock waves applied on particle surfaces.

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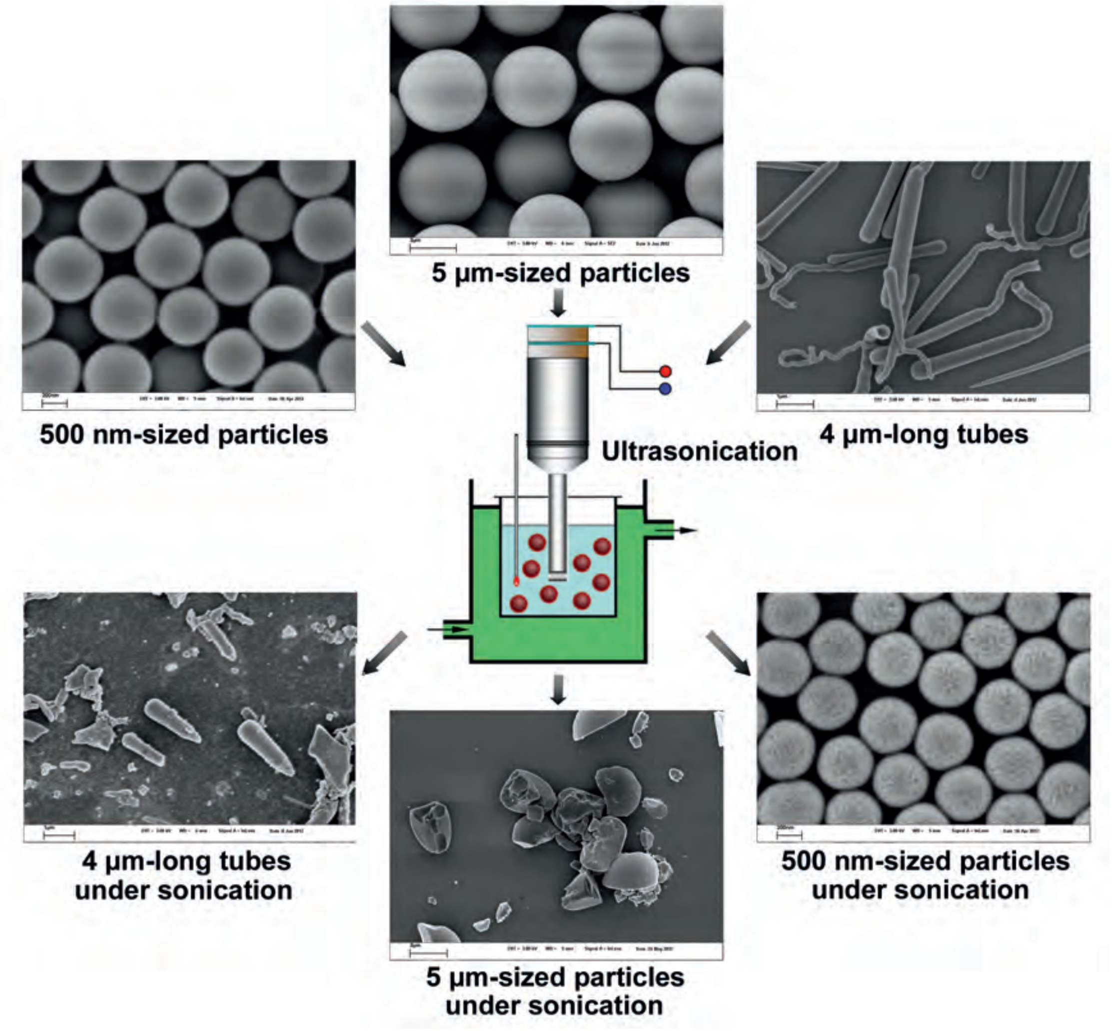

Figure 1: SEM Images of SiO_2 particles before and after ultrasonic treatment.

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Interfaces **3**, 417 (2011).

(QUASI) PLANAR INTERFACES – FLUID INTERFACES

Langmuir Monolayers as Model Systems to Study Interactions at Interfaces

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Aims

Monomolecular films at the air/water interface are interesting model systems to study different problems in biophysics or material science. Many parameters can be easily varied (composition, lateral packing density, surface pressure and area exposed to the medium, pH, salt concentrations, etc.). The interactions of dissolved biomolecules (DNA, peptides, enzymes) or nanoparticles **[1-3]** with lipid layers can be studied using surface sensitive methods. The investigation of beta-sheet forming peptides (cooperation with B. Koksch, FU Berlin) **[4, 5]** as well as of antimicrobial peptides (cooperation with J. Andrä, Research Center Borstel) is ongoing. The study of non-viral transfection systems (cooperation with B. Dobner, University of Halle) will also be continued **[6, 7]**. In this report, the main results of our work concerning β -sheet forming peptides, new lipids designed for non-viral transfection systems, the unprecedented two-dimensional structure of GlcNα1→6*myo*Ino-1-phosphodistearoylglycerol monolayers **[8]** as well as the interfacial self-assembly of polyoxometalate surfactants **[9]** will be described.

Selected Achievements

Triggers for β-Sheet Formation at the Hydrophobic/Hydrophilic Interface

Early stages in the aggregation process have recently been considered the cell toxic steps in amyloid diseases. Aiming at understanding various triggers for β-sheet formation (**Fig. 1**) such as peptide concentration, interactions with hydrophobic/hydrophilic interfaces, and metal ion complexation and their interplay, we investigated a set of model peptides at the air/water interface. These peptides existing in unfolded structures in bulk transform immediately to α-helices at the interface. Depending on the primary structure of the peptide, these intermediates can start to transform into β-sheets or can be extraordinarily stable compared to the fast aggregation of the peptides at similar concentrations in bulk. In general, the interface has the strongest effect on peptide conformation compared to high peptide concentrations or metal ions. Metal ions are able to prevent aggregation in bulk but not at the interface. The effectiveness of metal ion complexation to enhance the conformational transformation into β-sheets or to stabilize the α-helix is determined by the peptide primary sequence. For example, the binding of Zn^{2+} ions is strongly dependent on the possibility of chelate formation. Therefore, it additionally accelerates aggregation at the interface, when chelate formation is not possible in the α-helical state. Increased concentrations or a parallel arrangement of the α-helical intermediates are more effective triggers. Parallel alignment of highly concentrated α-helices (transition from 2D isotropic to 2D nematic state) at the interface always leads to aggregation. A better knowledge of these triggers may assist in understanding the fundamental mechanisms of common diseases related to amyloid formation (such as Alzheimer's disease, Parkinson's disease, or type II diabetes).

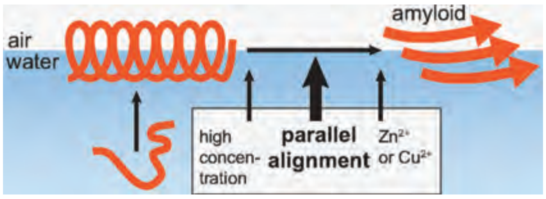

Fig. 1: Triggers for β-Sheet formation at the hydrophobic-hydrophilic interface: High concentration, in-Plane orientational order, and metal ion complexation.

Lipids for Gene Transfection: Important Features of Lipofection

To correlate structural characteristics of lipids with their transfection results is one important step to optimize the synthesis of cationic lipids (cooperation with B. Dobner, MLU Halle). For the first time, the binding of model DNA to lipid monolayers was quantified by IRRAS. As an example, the physical-chemical properties of two malonic acid amides with completely different gene transfer activities will be shortly described. The compounds exhibit the same head group structure (lysine linked via ethylenediamine) but different aliphatic chain patterns. We identified the key parameters explaining the different transfer activities. First of all, membrane fluidity plays an important role in lipofection. The miscibility behaviour with helper lipids, as cholesterol or DOPE, is another crucial parameter. In the present case, the lipid exhibiting strong van der Waals interactions between the saturated chains as well as strong head group interactions via hydrogen bonds forms a sub–gel like phase with high packing density and incorporates much less cholesterol. Despite the fact that in literature the 3D structures of the lipoplexes are considered of utmost importance, our results show that the transfection efficiency is not necessarily depending on it. Both lipids form lamellar phases without and with cholesterol. The addition of DNA does not change the phase type showing that non–lamellar phases are not crucial for high transfection efficiency. The amount of DNA bound to monolayers of these lipids is comparable at high and low pH values (at the same area per molecule) and is depending predominantly on the charge density in the monolayer (**Fig. 2**).

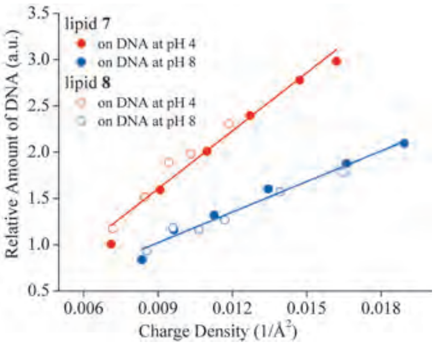

Fig. 2: Integrated reflectance-absorbance intensity of the phosphate bands of DNA bound to transfection lipids exhibiting the same head group structure but different aliphatic chain patterns (lipid 7: saturated chains, lipid 8: unsaturated chains) as function of the charge density at pH 4 and pH 8.

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Subgel Phase Structure in Monolayers of Glycosylphosphatidylinositol Glycolipids

Glycosylphosphatidylinositols (GPIs) are complex glycolipids playing key roles in a variety of biological processes. Yet, their membrane structure arrangement is still lacking a deep understanding. An unprecedented ordering in monolayers of the GlcNα1→6*myo*Ino-1-phosphodistearoylglycerol fragment **1** of GPIs was observed by GIXD. Several Bragg peaks in the mid-to-wide angle region (**Fig. 3A**) have been found. These peaks indicate a head group ordering (**Fig. 3B**) that was not observed in any of the previous studies on double-chain phospholipids including phospholipids with head groups that can be engaged in hydrogen bonding interactions. Indexing of all Bragg peaks revealed the existence of a supercell containing three molecules of **1** (**Fig. 3C**). This structure is reminiscent of the subgel phase structures observed in lipid dispersions after partial dehydration of the head groups during long incubation periods at low temperature. Here, the head group ordering is observed since a hydrogen bond network is formed that rigidifies the monolayer structure. The network of hydrogen bonds can be disrupted on highly concentrated urea subphases (urea acts as a chaotropic agent) leading to rotational disorder of the head groups and therefore to the loss of the molecular lattice and the restructuring of the chain lattice (**Fig. 3D-F**).

2D Supramolecular Structures of Polyoxometalates (POMs)

POMs and their supramolecular assemblies are materials of high relevance in different fields as catalysis, energy storage, and medicine. Using a new class of POM-based surfactants, 2D molecularly ordered supramolecular structures have been built at the air/water interface. The self-assembly of the POM units is driven by the lateral interactions between POM moieties. The crystalline structure formed by the polar head of the surfactants was quantitatively described for the first time (**Fig. 4**). The hydrocarbon chains are in a condensed-like state for POMs with chain length between C22 and C16.

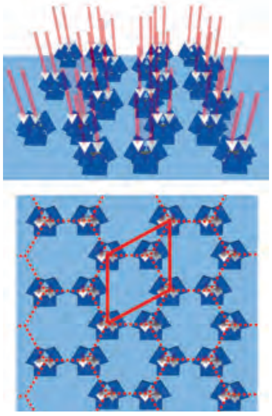

Fig. 4: Top: Side-view of a monolayer of the POM-Cn at the air/water interface. Bottom: Top-view: Hexagonal arrangement of the POM heads.

Future Plans

(1) Chemically modified phosphatidylinositols (PtdIns) and glycosylphosphatidylinositols (GPIs) will be studied in pure and mixed systems in cooperation with our department of biomolecular systems (P. Seeberger, D. Varon Silva) and the theory department (M. Santer). These studies are also performed with the vision to study enzymatic interactions.

(2) A new project studying the influence and function of chemically modified ceramides on the nanostructure and dynamics of stratum corneum model systems will be supported by the DFG. Our part concerns structural investigations of single and mixed 2D and 3D model systems.

(3) Physical-chemical studies of novel peptidomimetics based on the modification of amide bonds thus combining properties of α- and β-peptides (cooperation with L. Hartmann, department of biomolecular systems).

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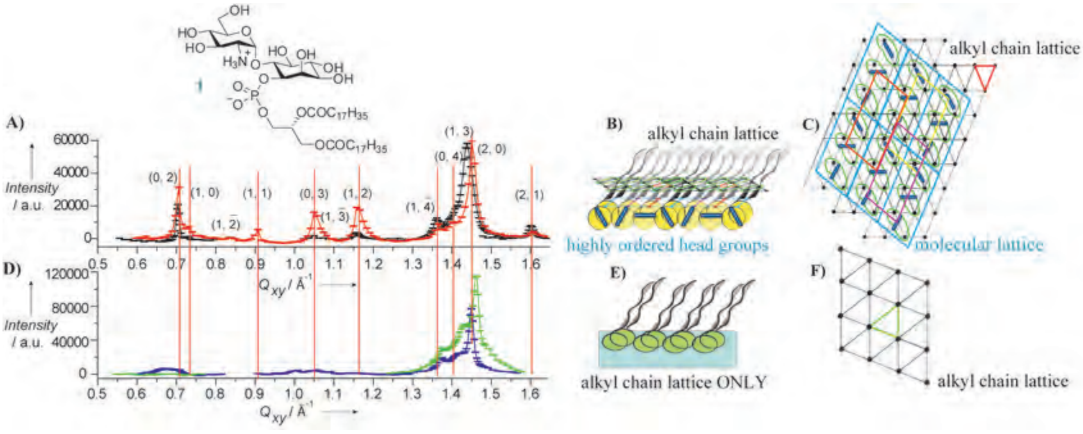

*Fig. 3: A) GIXD patterns of monolayers of **1** on PBS at 20 °C (2 mN/m - black line, and 30 mN/m - red line). B) Lateral view of the molecules at the air/water interface. C) Commensurable lattices describing the lateral order of the alkyl chains (black dots, repeating unit cell - red triangle) and of the entire molecules (repeating unit cell - blue parallelogram); repeating unit cells (red, yellow and magenta) linking molecules with the same head group orientation. D) GIXD patterns obtained on 5 M urea aqueous solution at 20 °C (2 mN/m - blue line and 30 mN/m - green line). E) Lateral view of the molecules at the air/water interface. F) Chain lattice (chains - black dots, unit cell – green triangle) on the urea aqueous solution.*

Interfacial Layer Structure of Adsorbed Ionic Surfactants at the Water-Hexane Interface

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1978: PhD, Physical Chemistry (Academy of Sciences, Berlin)
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1990/91: NCERC Fellow (University of Toronto with A.W. Neumann)
Since 1992: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
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Since 2012: President-elect of the International Association of Colloid and Interface Scientists (IACIS)

The group's main activities are focused on experimental and theoretical work on the thermodynamics and non-equilibrium properties of interfacial layers at water-air and water-oil interfaces **[1, 2]**. One of the long-term targets is to specify interfacial properties which correlate with the key parameters of corresponding foams and emulsions.

During the last few years we have been studying intensively the adsorption of surfactants at the water/oil interface. In contrast to the water/air interface, the interaction between adsorbing surfactants and the molecules of the oil phase is of importance and may change with the chain lengths of the surfactant and the oil, respectively. In order to avoid any transfer of surfactant across the water/oil interface we selected a homologous series of cationic surfactants, namely alkyl trimethyl ammonium bromides (C_nTAB, n = 10, 12, 14, 16), as this class of surfactants has been extensively investigated at the water/air interface.

The equilibrium adsorption isotherms of four members of this homologous series are shown in **Fig. 1** for the water/air and in **Fig. 2** for the water/hexane interface. In both graphs the experimental data are shown together with calculated model isotherms using a modified Frumkin adsorption model. This so-called Frumkin Ionic Compressibility model provides the best fitting of the experimental data, while other models show significantly larger deviations.

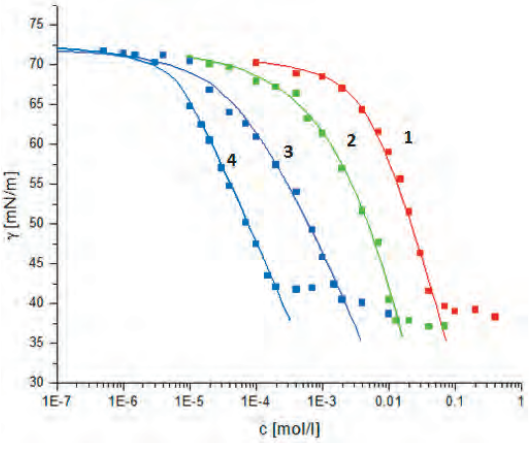


Fig. 1: Surface tension isotherms of $C_{10}TAB$ (1), $C_{12}TAB$ (2), $C_{14}TAB$ (3) and $C_{16}TAB$ (4) at the water/air surface; solutions were prepared in phosphate buffer (10 mM, pH 7); solid lines correspond to theoretical curves calculated with the Frumkin Ionic Compressibility model.

The experiments have been performed in 10 mM phosphate buffer for two reasons. First, in this way the ionic strength of the solutions was essentially the same for all surfactants at all studied concentrations. Moreover, experiments are under way for mixed protein/C_nTAB solutions, for which a fixed pH is required.

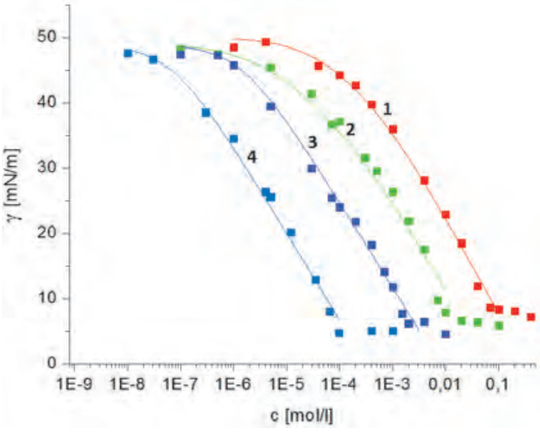


Fig. 2: Interfacial tension isotherms of $C_{10}TAB$ (1), $C_{12}TAB$ (2), $C_{14}TAB$ (3) and $C_{16}TAB$ (4) at the water/hexane interface; solutions were prepared in the phosphate buffer (10 mM, pH 7); solid lines correspond to theoretical curves calculated with the Frumkin Ionic Compressibility model.

The analysis of the isotherms provides information about the surface coverage of the interfacial layer, or the required area per adsorbed molecule, in dependence of the bulk concentration c. Note, ω is the molar area really occupied by one adsorbed molecule and not the geometric area available at the interface. As one can see in **Fig. 3** for the shortest chain surfactant $C_{10}TAB$, over the entire concentration range, the required area per surfactant molecule is larger at the water/hexane as compared to the water/air interface.

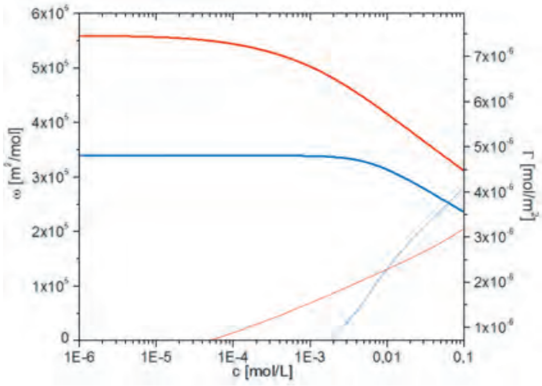


Fig. 3: $C1_0TAB$ adsorbed amount (thin lines) and molar area (thick lines) at the water/air surface (blue) and water/hexane interface (red) versus bulk concentration c; model calculations were performed with the Frumkin Ionic Compressibility model.

We can also note that a remarkable adsorption of the surfactant is already observed at the water/hexane interface at a much lower bulk concentration (10^{-4} mol/l) than at the water/air interface ($2x10^{-3}$ mol/l).

In contrast to this, the adsorption layers of the studied C_{16}TAB having the longest alkyl chain in this study, has a different structure. The adsorption at the water/hexane interface starts to be measurable at a bulk concentration less than 10^{-8} mol/l, while a real increase in the adsorbed amount at the water/air interface sets in only at a concentration of about 5×10^{-6} mol/l. At this concentration, the value of ω slowly decreases, i.e. the molecules change step by step their mean tilt angle. With increasing bulk concentration c, the molar areas and adsorbed amounts for both interfaces become almost identical, as we can see in **Fig. 4**.

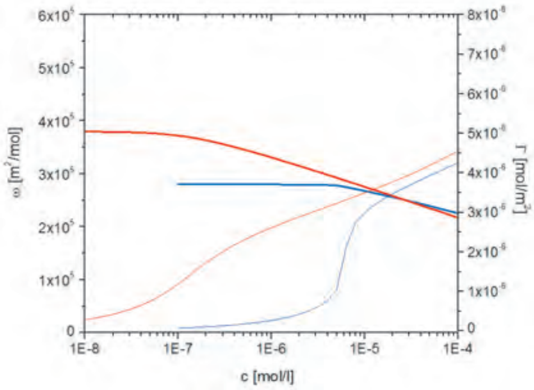
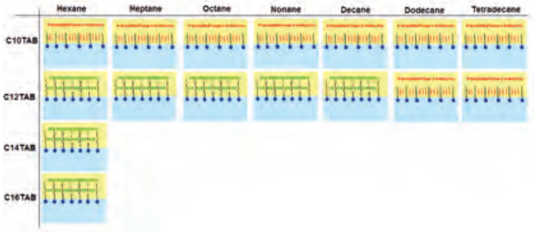


Fig. 4: C_{16}TAB adsorbed amount (thin lines) and molar area (thick lines) at the water/air surface (blue) and water/hexane interface (red) versus bulk concentration c; model calculations were performed with the Frumkin Ionic Compressibility model.

From these findings we can conclude that for the short chain C_{10}TAB the interfacial layer at the water/oil interface includes hexane molecules even at the highest surface coverage, i.e. close to the CMC. In contrast, for C_{16}TAB only at low surface coverage hexane molecules are intercalated into the interfacial layer and then get squeezed out at higher surface coverage due to the stronger interaction between the long alkyl chains of the surfactant molecules. For C_{12}TAB and C_{14}TAB a transition from the behavior of a short to a longer alkyl chain is observed.

Further investigations were made with alkanes of different chain lengths (from hexane to tetradecane) and the four members of the homologous surfactants C_nTAB in order to find out if there are transitions of the intercalation/squeezing out mechanism for the alkane molecules. The results can be summarized as shown in **Scheme 1**. While the interaction between adsorbed C_{10}TAB molecules is not strong enough to squeeze out neither short nor long alkane molecules, this is the case for C_{12}TAB for short alkanes. For dodecane and tetradecane, however, the interaction between alkane and surfactant is stronger than the mutual interaction between the surfactants, and hence the oil molecules remain intercalated.



Scheme 1: Molecular interaction between surfactants and oil molecules of different alkyl chain lengths

Complementary experiments were performed with surfactant solution drops formed in an alkane vapor atmosphere **[3, 4]**. Although alkane molecules are not amphiphilic, they adsorb and change significantly the adsorption of the surfactant molecules. Existing thermodynamic models allow a qualitative description. However, for a quantitative understanding a new thermodynamic model has to be developed that takes the co-adsorption of surfactant and oil molecules into account. The same physical picture might be applicable also to adsorbed layers at the interface between water and an oil bulk phase. This modelling work is presently underway.

Additional experiments were performed with drop profile and capillary pressure tensiometry to study the adsorption dynamics and dilational visco-elasticity of C_nTAB layers at the water/alkane interface **[5, 6]**. The results have shown that with the same set of thermodynamic parameters all dynamic properties can be described. Agreement between experiment and theory was achieved, however, only when choosing concentration dependent diffusion coefficients with physically rather unrealistic values. This also points to the fact that the models existing so far reflect only qualitatively the situation at the interface and combined with an improved thermodynamics, also refined relaxation mechanisms have to be developed to reach a quantitative understanding of the interfacial dynamics.

A new approach has been also started recently using CFD simulations of the processes happening at dynamic liquid interfaces **[7, 8]**. These simulations include also the description of growing and oscillating drops with a free interface and adsorption/desorption processes at this interface. Based on the Open-FOAM platform drop profiles under various conditions can be calculated. These results will give access to a modification of the Gauss-Laplace-Equation valid also in a respective range of Reynolds numbers and a specified capillary geometry for forming the drops.

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Phase Transitions and Transport Phenomena at Solid/Air Interfaces

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We are interested in a better understanding of nucleation/aggregation phenomena and in the coupling between volume flow and surface Marangoni-flow caused by interfacial energy gradients. Nucleation and aggregation phenomena are ubiquitous (from cloud formation to metallurgy). Liquid flows induced by surface tension gradients are also widely relevant e.g. for ink jet printing. Our primary aim is a better fundamental scientific understanding of these issues.

Nucleation and growth studies are performed within an international graduate school (funded by DFG) in collaboration with universities in the Berlin area and academic partners in the US (NC State University). The Marangoni-flow activites are embedded in a collaboration with Twente University (NL). A "by-product" of this collaboration is a successful study on nanobubbles **[1]**. Based on our expertise on nucleation, growth and Marangoni-induced transport/flow, we further started collaborations with French research groups on pit corrosion (CEA, Saclay) and on separation chemistry (ICSM, Marcoule). The focus is on basic research but there are also activities motivated by application. We collaborate with industry (LAM Research) to investigate the fundamentals of Marangoni cleaning, and we use our knowledge to optimize the architecture of molecularly thin films in organic solar cells (project funded by the BMBF).

Line Tension

Line tension effects can become relevant when interfacial energies are substantial compared to volume free energy contributions. This only occurs for very small, nano size sessile drops (or adsorbed aggregates). Minimizing the total free energy leads size-dependently to different equilibrium shapes e.g. the equilibrium contact angles depend on size. To first order the effect can be parameterized with the curvature of the contact line, hence "line tension". Experimental verifications of line tension effects are scarce. We measured this effect **[2]** with very small aggregates of C60 on various molecularly smooth surfaces (**Fig. 1**).

Although theoretically predicted since a long time, a general palpable theory of line tension based on intermolecular interactions is still missing. We develop such an approach. The predicted variation of the shape with size is in agreement with the experimental results (**Fig. 1**). Essentially, a line tension effect occurs when the variation of the interfacial force field contributions with drop size are comparable to the volume force field contributions. The variation of the interfacial force field is dominated by contributions from the contact line region, hence "line" tension. Line tension effects can be regarded as resulting from a locally varying, size-dependent disjoining pressure.

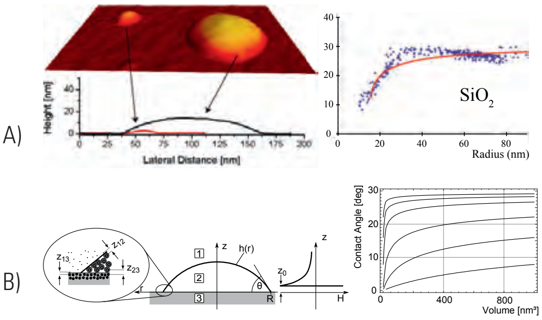

Fig. 1: A) AFM image of small aggregates and measured variation of their contact angle area with size [2]. B) Model and theoretical results.

Heterogeneous Nucleation

First order phase transitions implicate the formation of an interface between the old and the new, emerging phase. This causes a supplemental energy, a nucleation barrier for the transition. The nucleation is heterogeneous when the emerging phase is in contact with other (inert) phases in addition to the interface between old and new phase. Compared to the homogeneous case the energy barrier for heterogeneous nucleation is lower. This lowering is parameterized usually only by the contact angle between emerging and inert surface. However this single parameter approach only works for simple planar geometries. If the topography between emerging phase and inert template is non-planar, the nucleation barriers and paths also depend on the topographic details of the template.

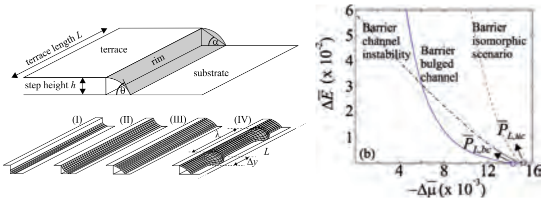

Fig. 3: Nucleation path of edge melting with a transition from a plain to a bulged channel (the bulges grow into macroscopic drops). Comparison between the nucleation barriers for various morphologies.

Experimental investigations and theoretical calculations **[3]** with nucleation templates with edges and grooves explicitly reveal how the nucleation barriers and pathways depend on the height and length of steps/grooves. In addition we find that with templates of reduced symmetry (e. g. long steps or grooves), the nucleation path with the lowest energy may be non-isomorphic. That means, as during the evolution from subcritical to supercritical (bulk) volumes, the new phase nucleus changes its shape (e.g. from a plain channel to bulges, (**Fig. 3**)). Up to now, all theoretical nucleation scenarios always assumed isomorphic volume growth for the lowest energy nucleation path.

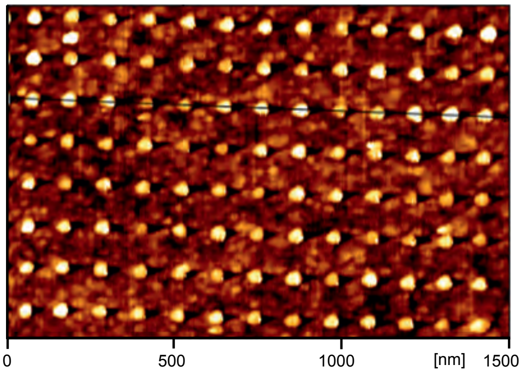

Fig. 4: C60 aggregates on nano-patterned SiO_2-substrate

Heterogeneous nucleation is also investigated with planar solid substrates that were pre-structured with an array of nano-indents. Unexpectedly it is observed that upon spin casting from solution precipitated C60 aggregates form preferentially in the dents (**Fig. 4**). The dents are less than 1nm deep and the estimated reduction of the nucleation barrier by the dent geometry is quite small. To gain better insight into the spatio-temporal evolution of the nonvolatile solute (C60) during the film thinning – which in the end leads to the observed phenomena – the spin casting process itself is analysed theoretically **[4]**.

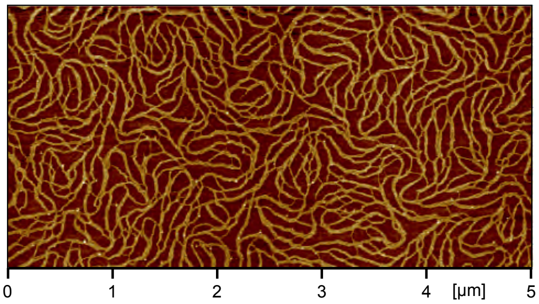

Fig. 5: Phytalocyanine net structures (height≈1.5nm)

Phtalocyanine-Films for Organic Solar Cells

Molecularly thin films of Phtalocyanines (PC) were prepared with structures optimized for Heterojunction Organic Solar Cells (OSC) **[5]**. The PCs form interesting films with ribbon-like bundled multilayer net structures (**Fig. 5**). A detailed experimental analysis and model calculations reveal the nucleation and growth processes leading to the observed structures. With these films functioning OSCs were prepared via solution processing **[6]**.

Interfacial Flow and Drop-Drop Coalescence

Upon lateral contact, sessile drops of miscible liquids are expected to merge rapidly due to capillary forces. With different liquids in both drops, upon contact, surface tension gradients form in the connecting region. This induces a Marangoni flow, which can unexpectedly cause a long delay of the drop coalescence. The main drop bodies remain separated while connected via a thin neck through which the drops exchange liquid. The delay of the coalescence is now finally understood theoretically **[7]**. The drop-drop coalescence system is now used as an experimental and theoretical model system to investigate the impact of surficial Marangoni flows on the hydrodynamics of thin films for different cases, such as surface tension gradients caused by local evaporation (coffee stain effect) or vapour adsorption.

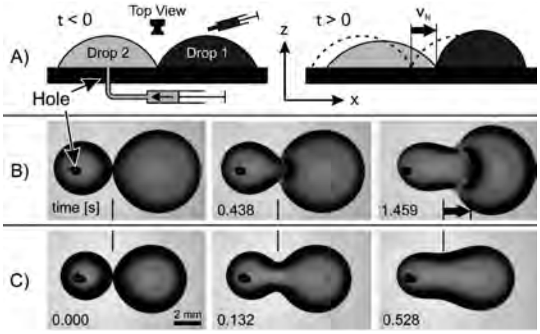

Fig. 4: A) Schematics of the experimental setup/procedure;
B) non-coalescent twin drop movement (different, miscible liquids);
C) instantaneous coalescence (identical liquids).

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NON-PLANAR INTERFACES

Active Interfaces and Coatings

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Feedback Active Coatings

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 **[1-6]**. 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 like bio- or sensor activity.

The introduction of only few percents of microgel particles containing a ''green'' corrosion inhibitor allows significant improvement of the corrosion protection properties of a coating **[1]**. The effect can be attributed to improvement of the barrier properties of the coating as well as to the action of the corrosion inhibitor, which totally suppresses the corrosion process in the local area of the damage. Usage of microgels is very advantageous, since they combine the properties of both liquids and solids. The polymeric framework of the crosslinked polymeric network supplies the system with the mechanical strength, while the corrosion inhibitor retains its mobility and can be delivered to the metal surface when the coating is damaged. The synthesis of microgels is comparatively easy and can be performed in a one pot process, which increases the potential for up-scaling.

Silica armoured polystyrene composite nanocontainers were filled with 5, 10 or 20 wt-% of 8-hydroxyquinoline **[2]**. The aim of our work is to introduce a new type of containers based on Pickering emulsions (**Fig. 1**) as one of the controlled delivery and release tools for further application for uptake and release of the potentially various types of active materials in both delivery systems and multifunctional feedback active coatings. The approach was employed in self-healing coatings in order to demonstrate the application potential of the proposed new type of nanocontainers. Especially the design of multifunctional container components is crucial for this work, since it allows for a reduction of fabrication steps and involved reagents for their synthesis.

A method to spontaneously form hybrid nano-structures consisting of ceria nanoparticles supported on a porous silica colloid was reported in **[3]**. The structures have high surface area and can be used to adsorb useful molecules for future release. Spontaneous emulsification, which requires neither template nor externally applied energy, has been shown to be a green method to generate silica nanostructures that could find future use either in corrosion prevention or, perhaps, in other fields as easily recoverable catalyst support.

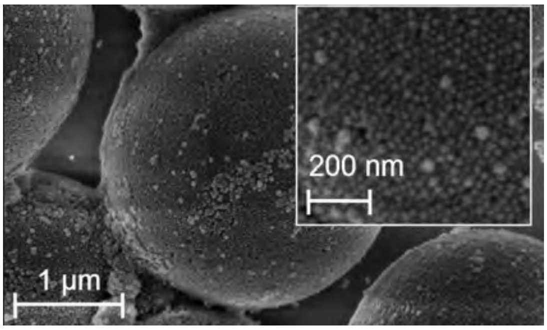

Fig. 1: SEM micrographs of silica-8-hydroxyquinoline composite containers based on Pickering emulsions [3].

The mesoporosity, monodispersity and spherical morphology of the studied silica nanoparticles favour their application as nanoreservoirs for corrosion inhibition **[4]**. The incorporated mechanically stable nanocarriers block the micro-pores, cracks and areas with low cross-link density in the passive SiO_x/ZrO_x coating film and improve its physical barrier properties. Furthermore, due to the pH-stimulated release of inhibitor during the corrosion process well pronounced active self-healing was provided.

A polyelectrolyte coating of poly-*l*-histidine and poly(methacrylic acid) was prepared and shown to be effective for sustained release of negatively charged species under physiological conditions **[5]**. This complex demonstrated pH-dependent release with low levels of sustained release at pH = 7-8. Controlled release on the microgram scale over 25 days was shown at physiological pH, which is advantageous and necessary for the desired *in vivo* effect, i.e. signalling of osteoblasts to the implant surface. Coatings capable of dissolution under physiological conditions are well-suited to application on porous titanium surfaces because their removal from the surface exposes the porous structure to cells, potentially allowing for greater osseointegration of the titanium implants. Stable microspheres loaded with vitamin E can be obtained by vitamin emulsification in the gum acacia solution using ultrasound treatment **[6]**. The obtained microcapsules were embedded into a cross-linked Ca-alginate film forming a model cutaneous drug delivery system. Vitamin E release kinetics from the Ca-alginate film with entrapped microspheres is essentially more sustained, especially in comparison with the release of free vitamin distributed in the polymer film.

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Sonication as a Tool for Surface Modification

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 **[7-9]**. The surface of the ultrasonically produced nanomaterials can be changed by decorating it with suitable hydrophilic and hydrophobic organic moieties.

Cavitation at the solid surface normally begins with a nucleation process, in which the defects or assembled molecules located at a liquid-solid interface act as nucleation centers and are actively involved in the evolution of the cavitation bubbles. A mixture of octadecylphosphonic acid and octadecanethiol was stamped on the Si wafer coated with different thicknesses of aluminium layer (20-500 nm) **[7]**. The height values between hydrophobic and hydrophilic surfaces were reduced up to 3 nm in order to equilibrate the contribution of both surfaces to the nucleation process. Only the hydrophobic surfaces provided the nucleation centers at the initial stage of sonication (up to 40 min). SEM and AFM microscopy studies of the surface topology after sonication proved that cavitation bubbles are far more likely to nucleate at the hydrophobic surface (**Fig. 2**).

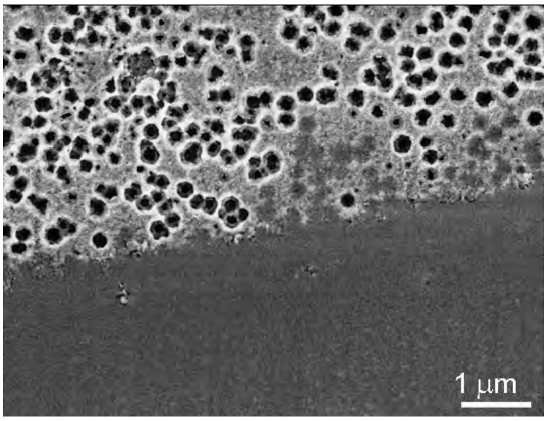

Fig. 2: SEM micrographs of the patterned Al sample after 10 min of sonication Upper part is the hydrophobized part [7].

Active defects (pits) formed only on the hydrophobic surface at the initial stage of ultrasonic treatment contribute to nucleation of cavitation bubbles during the increase of sonication time. High intensity ultrasonic irradiation induces the formation of an interfacial gas layer at the solid surface immersed in different liquid media (water saturated with different gases, such as argon, nitrogen or carbon dioxide) by accelerating the adsorption of dissolved gas **[8]**. Subsequently, the gas rearranges in diverse nano- or microstructures which take further part in the cavitation process. The presence of argon and nitrogen in the liquid medium accelerates the surface cavitation keeping the response selective on the patterned surfaces. By varying the gas adsorption time it is possible to accelerate or to slow down heterogeneous cavitation. Likely a secondary nucleation mechanism takes place in this system, whereas the gas can be trapped (forming assembled molecules) into the defects formed and initiates the following growth of new cavitation bubbles. We also observed that at longer sonication times (more than 40 min), the thermal mechanism of the formation of porous metal surfaces prevails over the cavitation effects **[9]**.

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NON-PLANAR INTERFACES

Nanotechnology and Optical Manipulations of Capsules and Films

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Aims

Research goals of the nano-bio-interfaces group are targeted to use the basic principles of physical chemistry for designing spherical and planar interfaces for interaction with living cells. Such approaches are envisioned to enable investigation of fundamental processes in cell biology: protein trafficking, the surface presentation of peptides, aggregation state of proteins as well as design of new interfaces for patterning and re-configurable interfaces for cell cultures. Both spherical and planar interfaces and methods are used for investigation and advanced characterization. We are also designing new Raman based sensors and amplifiers for label-free imaging.

The group is also using principles of self-assembly for designing a next generation of carriers, multicompartment and anisotropic carriers as well as gradient surfaces.

Present Work

Currently, we are continuing our work on probing polymeric and lipid membrane permeability. Using the obtained knowledge, we are gaining insights into the structure and functions of proteins at the surface of cells. These principles are also used for inducing release from red blood cells (**Fig. 1**). It was found in our studies, that opto-nanoporation can be also used for release of molecules from red blood cells.

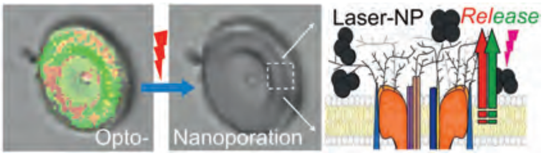

Fig. 1: Investigation of the permeability and release of molecules from red blood cells using opto-nano poration.

Raman spectroscopy has been used to confirm binding of gold nanoparticles onto lipid membrane and oligosaccharides and proteins located on the membrane of red blood cells. Control experiments have been conducted to exclude thermal and photo-bleaching. To the best of our knowledge, this is one of the first accounts of active release from red blood cells.

Intracellular incorporation of probes is extended to include label-free (Raman based) sensors. Their performance is assessed by performing label-free imaging of cells.

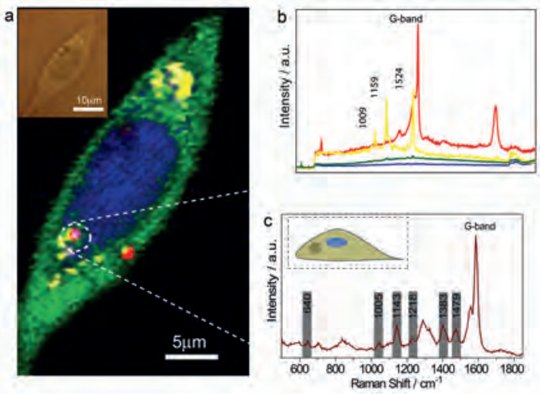

Fig. 2: Raman micro-imaging and mapping of molecular features of SiO_2, silica (red) particles functionalized with gold nanoparticles inside living cells.

Here, we are actively using Raman spectroscopy and microscopy for investigation of molecular features of molecules inside living cells (**Fig. 2**). Using nanoparticles and silica colloidal probes we have designed intracellular probes for label-free imaging and observed signal amplification.

It can be seen from **Fig. 2** that cytosol and nucleus of a cell can be also imaged based on label-free scattering. The designed sensors are quite efficient, so that even application of light with intensity comparable to that of sun produced detectable label-free scattering signals.

We have also pursued a new approach towards controlled patterning by using a simple method of adsorbing gold nanoparticles at the surface of soft films. These become stiffer thus controlling protrusion and, and therefore, masking the particles which can be later on patterned with controlled patchiness. Using such an approach fabrication of anisotropic multicompartment constructs is also possible. Peculiarly, using the same approach of adsorbing nanoparticles film stiffness is increased, improving cell adhesion on the surface. This is particularly useful for seeding cells and designing active bio-interfaces.

Interestingly, application of gold nanoparticles has been beneficial in connection with poly-L-lysine/hyaluronic acid (PLL/HA) films. These films are particularly attractive due their reservoir-like properties. However, they are also quite soft - an undesirable property for growing cells. Application of gold nanoparticles has been shown to enhance mechanical properties of such films making them stiffer. This very property has been also used in our research to design novel means of controlling patchiness of multicompartment capsules and particles. Application of gold nanoparticles strengthens the films, thus enabling controlled embedding of capsules and leading to fabrication of capsules with controlled patchiness.

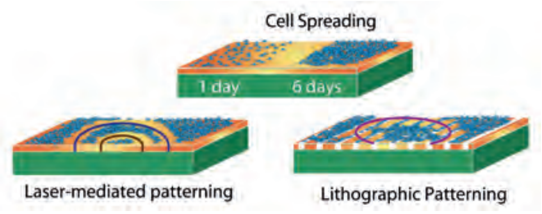

Fig. 3: Cell-patterning by laser-nanoparticle interaction.

Active bio-interfaces have been tested by controlled laser-nanoparticle induced patterning of cells (**Fig. 3**). In this direction remotely controlled methods were employed, and cell detachment, patterning, and regrowth were investigated. Natural continuation of this work is seen on self-assembly of nanoparticles and polymeric films.

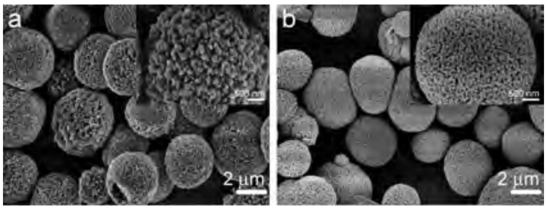

Fig. 4: Calcium carbonate biocompatible microparticles with incorporated gold nanoparticles for efficient label-free sensing.

One of the directions of research concerns development of methods for enhancement of label-free Raman signals using colloidal and interfacial modification. Figure 4 shows calcium carbonate porous microparticles before and after functionalization with gold nanoparticles. Subsequently, calcium carbonate microparticles functionalized with gold nanoparticles were used for detection of such biomarkers as glucose.

Other research areas include development of carriers for enzyme-catalyzed reactions and investigation of mechanical properties of polymeric capsules and films as well as their interaction with cells. In the former case we are developing means of protection of enzymes as well as using enzymes for intracellular degradation of capsules. In the latter case we are trying to understand mechanobiology and develop mechanically stable carriers based on understanding of these processes.

Future Goals

Using interfacial methods, we are planning to:

- design carriers for enzyme-catalyzed reactions in which enzymes are protected, while the substrate freely circulates for enzyme-catalyzed reactions;
- further develop reconfigurable and adjustable interfaces for controlling and patterning of cells;
- design gradient coatings and use them for investigation of capsule-surface interaction, motion, positioning;
- using interfacial approaches, investigate mechano-biology of microcapsules relevant for in-vivo delivery;
- develop novel and advanced anisotropic carriers and capsules;
- design novel Raman based sensors and amplifiers based on nanoparticle self-assembly. Use these probes for intracellular imaging and sensing.

Establishing an extensive network of collaborators is a istinct feature of our work; in this regard we collaborate with Department of Biomaterials, MPI of Biophysical Chem., Jacobs University of Bremen, University of Bayreuth, Greifswald University, University of Ghent, Harvard University, Charite-Berlin Clinic, Queen Mary University of London, and University of Marburg.

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