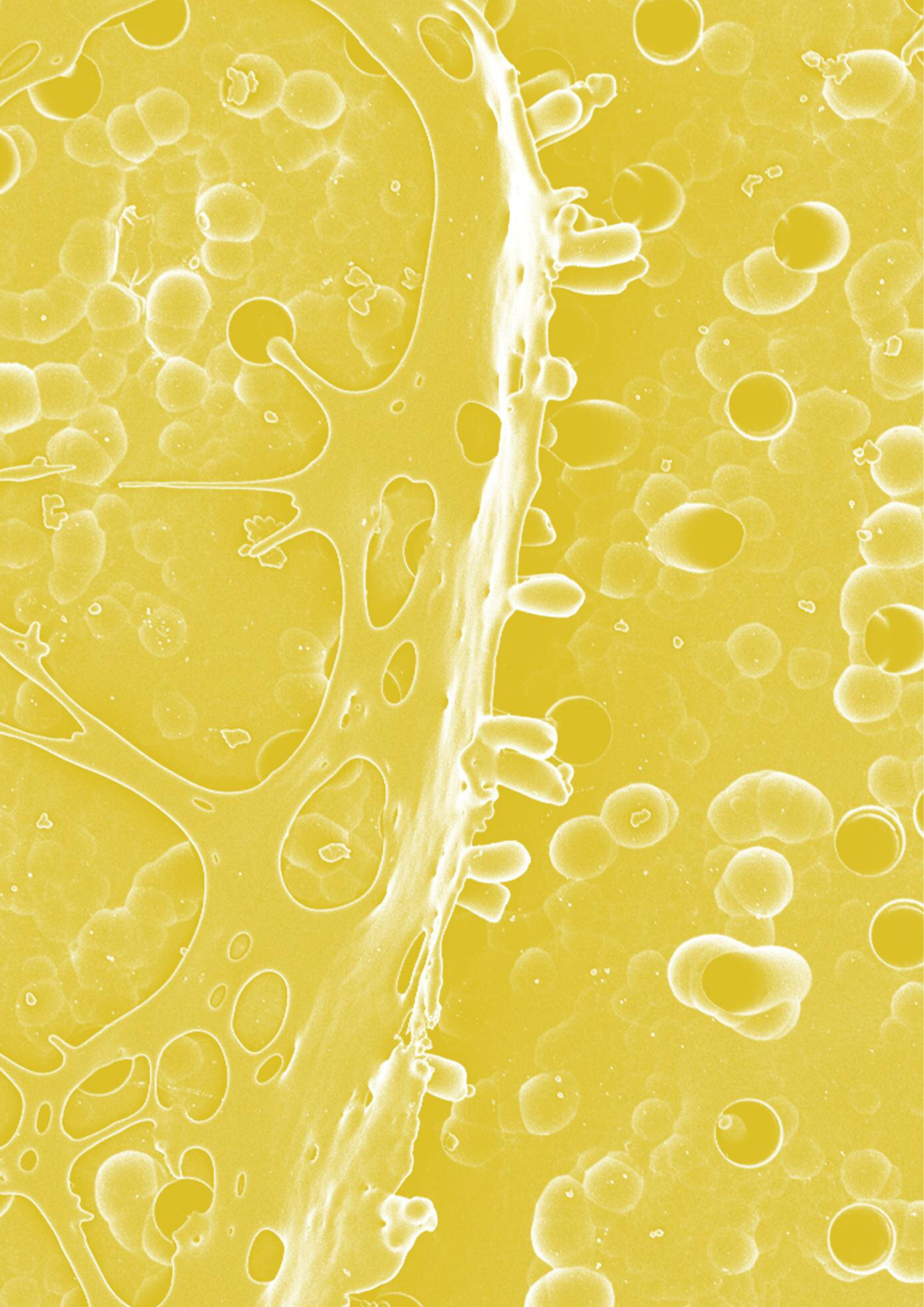

→ (Quasi) Planar Interfaces – Fluid Interfaces
→ Solid Interfaces
→ Non-Planar Interfaces
→ International Joint Laboratory
→ MPI-NIMS International Joint Laboratory

INTERFACES

Research in the Department of Interfaces

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1971: Diploma, Physics (University Göttingen)
Thesis: Messungen der absoluten Polarisation optischer Übergänge an Molekülen und Molekülkomplexen in Flüssig-Kristallinen Lösungsmitteln
1974: PhD, Physics (University Göttingen, Max-Planck-Institut für Biophysikalische Chemie, A. Weller, E. Sackmann)
Thesis: Lokalisierte und delokalisierte Triplettzustände in Einkristallen von Elektron-Donor-Akzeptor-Komplexen: ESR- und emissionsspektroskopische Untersuchungen zwischen 4K und 300K
1974-1975: Postdoc (IBM San Jose)
1975: Research Assistant (University of Ulm)
1978: Habilitation, Physics (University of Ulm) Thesis: Transporteigenschaften und Phasenübergänge in organischen Charge-Transfer Kristallen
1978-1981: Scientific Coworker (Dornier-System, Friedrichshafen)
1981: Associate Professor C3, Experimental Physics (TU München)
1987: Chair C4, Physical Chemistry, (University of Mainz)
Since 1993: Director and Scientific Member (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 1995: Professor, Physics and Physical Chemistry (University Potsdam)
Since 2001: Honorary Professor (Zheijang University, Hangzhou)
Since 2004: Honorary Professor (Fudan University, Shanghai)
Since 2006: Honorary Professor (Institute of Chemistry at the Chinese Academy of Sciences, Beijing)

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 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 4 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. One exception may be studies of ion binding to interfaces where the water structure is most important and where thus even simple charged molecules are good models.

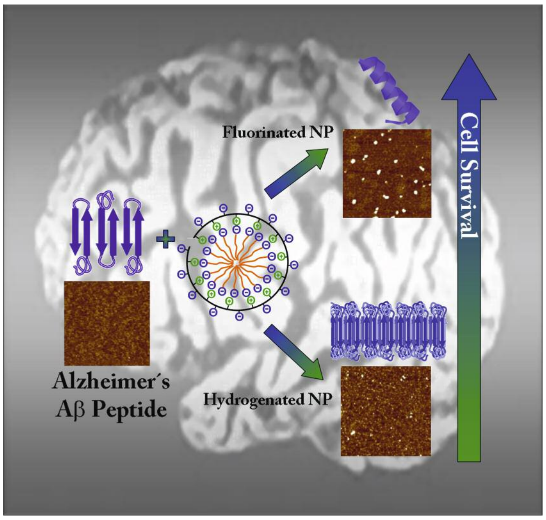
On the other hand the mission is also to concentrate on basic science and therefore schemes had to be developed to transfer technology and knowledge to groups and partners oriented towards application.

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 eight 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

The specially advanced expertise and methology 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:

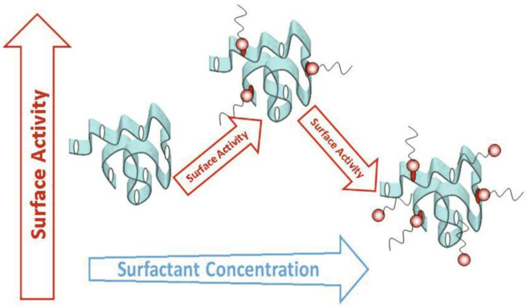


Dynamic fluorinated nanoparticles (NPs) induce α-helix-rich structures in Aβ peptides, prevent aggregation and increase viability of human neuroblastoma cells treated with Aβ oligomeric species, whereas their hydrogenated analogues lead to β-sheet formation and fibrillation.

- The formation of beta sheets of specifically designed peptides in presence of different divalent cations has been studied in 2D and 3D models, revealing the importance of the interface (cooperation Prof. B. Koksch, FU Berlin).
- The interaction of antimicrobial peptides with membranes has been shown to depend on membrane charge which is most important for their cell specific activity. (coop. Dr. J. Andrä, FZ Borstel).
- As an extension of prior studies with planar interfaces it is shown that fluorinated nanoparticles can induce a higher α-helical content of the amyloid-β-peptide (1-42). This reduces their propensity to form fibrils, the precursors of plaques in Alzheimer's disease (coop. Proff. Coelho, Pereira, Univ. Porto; Prof. Sareiva, Inst.Mol.Cell.Biol. Porto; and Dr. K. Tauer, MPIKG, dept. colloid chem.)
- New zwitterionic phospholipid membranes have been developed that appear most suitable for DNA transfection (coop. Prof. Dobner, Univ. Halle)
- The interaction of magnetic nanoparticles with temperature and salt sensitive shell has been studied at interfaces. It is shown that they can be bound to the interface up to a critical pressure and above this, depending on temperature, may form a multilayer arrangement or dissolve in the subphase (coop. Prof. D. Wang, now Univ. Adelaide).

The previous studies on enzymes

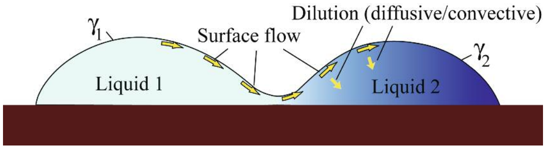
at interfaces have been interrupted due to a lack of cooperation partners and will be resumed now in cooperation with the department Biomolecular Systems.



The addition of ionic surfactants initially increases the surface activity due to ionic interaction. Further increase in surfactant concentration decreases the surface activity of the resulting complex due to hydrophobic interaction.

The group of *R. Miller* has been continuing their studies of detergent/ protein interactions at interfaces using as models β-casein and β-lactoglobulin (coop. Donetsk, Nestle). Their surface activity depends on detergent/ protein ratio, and this can also be understood by means of a newly developed model. The model also explains well surface rheological data as well as the detergent dependence of foam stability, which has been studied by the group for these systems (coop. Univ. Sofia). As, initially a by-product, they could show that alcanes can form a continuous film at the air/ water interface, and this film can be characterized via surface tension studies and ellipsometry.

The group of *H. Riegler* has very much refined their optical and force microscopic observations of nucleation and growth of liquid bubbles and solid phases on structured surfaces, thus yielding most quantitative data on interfacial interactions. They thus could demonstrate how nanosized roughness influences liquid droplet formation of fullerenes. They show that the contact angle of small droplets depends on their size and derive a model from which they obtain the line tension. From the coverage dependence of phase transitions of alkanes and alcohols on SiO_2 they can conclude on interfacial interactions, and these differ for the two types of compounds due to different head group hydration. They demonstrate that melting at steps on a surface may proceed by a nucleation and growth scenario which differs in morphology from that on flat surfaces or in bulk (coop. dept. Theory & Bio-Systems). 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). They also employ their expertise in controlling nucleation and growth in nano-dimensions in a collaborative project (coop. Helmholtz Center Berlin) to fabricate heterojunction organic photovoltaic cells.



The schematic shows how the coalescence of two sessile drops of different but completely miscible liquids is delayed by a surface flow ("Marangoni" flow) that is caused by the difference in the surface tensions of the liquids. The surface flow "pushes" away drop 2 from drop 1, keeping their main body separated. Liquid 1 that is advected onto the surface of drop 2 with the surface flow is continuously diluted. Thus a temporary steady state surface tension gradient is established. This can delay the coalescence by many orders of magnitude compared to the coalescence of drops with identical liquids driven solely by capillary forces (many seconds compared to milliseconds).

II. 2 Non-Planar Interfaces

The group of *T. Nakanishi* has been synthesizing fullerenes with 2 or 3 specially designed aliphatic tails. Because the fullerene and the aliphatic moiety are immiscible they tend to microphase separate in a similar way as tails and head groups of classical amphiphiles. Therefore they also tend to form a zoo of lamellar or micellar phases which in addition depend of the type of organic solvent. The group has now elucidated this richness of phases and stabilized them via cross-linkable aliphatic tails. The high π-electron density contributed by the fullerenes also enables a high charge carrier mobility. As an interesting future direction it has been possible to attach chains disfavouring lamellar phases and thus obtain a liquid isotropic phase with viscosity like honey. This still exhibits a considerable charge carrier mobility (10^{-3} $cm^2/V*sec$) which may be sufficient for some photovoltaic applications. The work of the group has been terminated, and 3 members have joined *T. Nakanishi* who has returned to the National Institute of Materials Science in Tsukuba. This also guarantees that some work can be continued in cooperation, especially that where carbon nanotubes were functionalized like fullerenes and where flower-like metalized structures are used for further interfacial studies like for biosensing and Resonance Raman spectroscopy.

The group of *D. Shchukin* has been engaged in basically 2 directions.

(A) Development of stimuli sensitive nanocontainers to be embedded in enabling the development of self-repairing coatings.

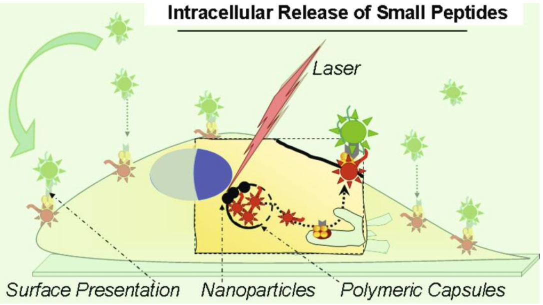
(B) Development of sonochemistry as a tool for surface and nanoparticle modification.

Under (A) nanotubular (halloysite) or nanoporous inorganic carriers were developed that via a polyelectrolyte multilayer shell exhibited stimuli sensitive release of incorporated corrosion inhibitors. After embedment in a coating they then could show that the different local pH near a defect can cause inhibitor release and thus annealing. The release can additionally or alternatively be effected by laser light. These studies are most promising for applications and will be pursued partly removed from the institute's main stream.

The activities under (B) were initially aiming to develop new types of nanoparticles by ultrasound or to arrange these particles. This has been rather successful, e.g. to prepare amalgamated Au-Ag particles, to arrange nanoparticles in clays or to fabricate highly luminescent ZnO particles by injecting Mg into them. It also became apparent, and we could develop corresponding models, that the process could be controlled by different surfactants that coat nanoparticles as well as the cavitation bubble formed during sonication. Therefore a new direction was taken up studying sonochemistry at solid surfaces. 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.

The group of *A. Skirtach* has been most successful in developing Au nanoparticle aggregate insertion in membranes for local heating remotely via bio-friendly laser light. As one of the outstanding experiments they could encapsulate a signal peptide in a polymeric capsule that was introduced into a lymphocyte. This peptide could then be released remotely, and the signal cascade leading to a presentation of a specific antibody complex could be followed and quantified locally as a function of time.

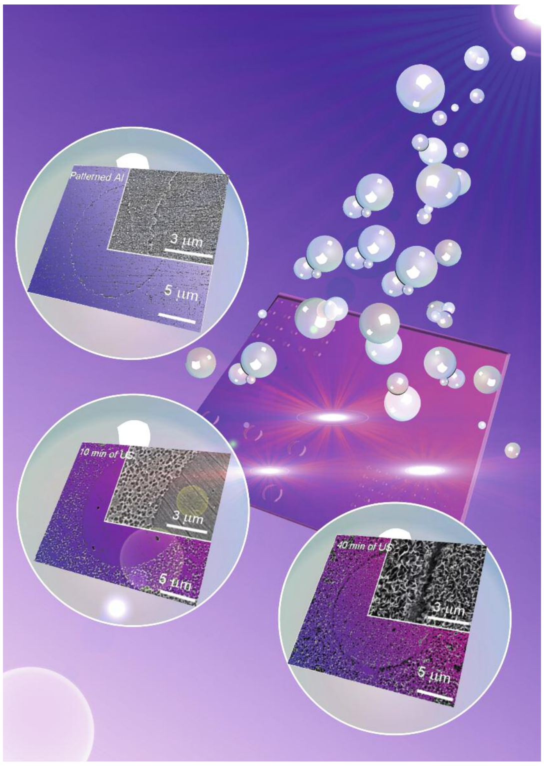
Another successful development of the group concerns multicompartment capsules and accomplishment of mechanically induced and directionally specific release.



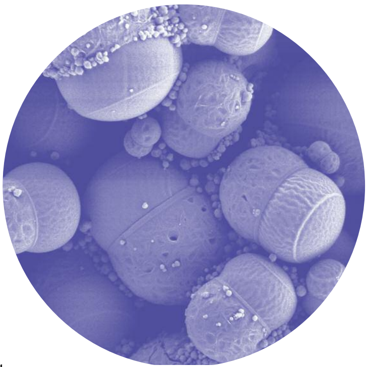
The group of *D. Wang* has had much success developing a simple method of fabricating Au nanoparticles of very uniform size and shape. It basically exists of modifying the well-established Turkevich method by adding trace amounts of silver nitrate. Thus nucleation of Au was facilitated and the multiple role of citrate as buffer, reducing and nucleating agent could be separated. They could prepare Janus particles by a simple procedure ,coating PS particles by polyelectrolyte multilayers. Swelling of the particles by solvent exchange then leads to protrusions (here only one) and thus snowman like shapes are obtained. Coating of nanoparticles by pH or temperature sensitive polymers is shown to lead to phase transfer between water, oil and also a hydrogel phase. Via control of electrostatic interactions and the assembly kinetics they demonstrated that compact spheres, discs or fibrillar arrangements of CdTe nanoparticles coated by L-cystein can be made. The group has been terminated after the group leader *D. Wang* accepted a professorship in Adelaide.

The international laboratory with the Chinese Academy of Sciences in Beijing led by *J.B. Li* has been active studying structure formation as well as active transport of capsules. Using dipeptides with the phenylanaline motif they showed that a zoo of self-assembled structures exists: vesicles, nanotubes or nanowires. Transitions between these structures were shown to be initiated, e.g. by pH, followed optically and described theoretically. The structures are just functionalized further to enable their manipulation by light and other electromagnetic fields. They also isolated microtubules with micron-sized capsules attached and followed their movement on a surface with fixed motor proteins. The velocity does not depend on the size of the cargo, typical for a stepper motor.

The joint German-French lab on sonochemistry has produced its first publications in the last 2 years. 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. In accordance with a derived nucleation and growth model it was shown with micropatterned surfaces that the process predominates on hydrophobic surface areas and the impact is due to a microjet resulting from bubble collapse.



Ultrasonically nano- and microbubbles are preferentially formed on hydrophobic parts of a patterned surface (outside the circular areas). Their collapse causes corruptions at early times (10 minutes) only on hydrophobic areas, later over the whole surface.



In first examples towards ion separation it was shown that ultrasound can be used for selective leaching of glasses where the process starts at microcracks. It can also be used as a clean, well-controlled and fast way of flotation, a traditional way of ion separation. In this case the selectivity follows the Hofmeister series indicating the importance of hydration forces.

III. Future Development

Major changes of staff in the last 2 years have been:

- *D. Wang* accepted the offer of a professor position at the Ian Wark Institute in Adelaide and moved there in July 2010.
- The two international laboratories with the NIMS in Tsukuba, Japan and with the CAS in Beijing, China have been terminated in March and December 2010, respectively, and the two group leaders *T. Nakanishi* and *J.B. Li* returned for permanent to their home institutions.

These changes were as expected and in line with the intention to drastically shrink the department size. Still, in all cases there are continuing collaborations with people remaining in the institute and postdocs joining the leaving group leaders, and these are expected to persist at least through 2011.

With these and some other measures the department has been shrinking from 80 persons to about 50 and in the next year is expected to approach the targeted 40 persons. This has been the aim in view of my desire to retire as director. However, as it has not yet been possible to install a 5th director I have extended my contract in accordance with my colleagues and the authorities of the Max Planck Society by three years or until a successor takes over. However, the budget has been drastically reduced, and also space was required by the other departments. Therefore shrinking was the optimum solution.

In view of this there are no realistic long-term visions for the department as a whole. Instead the aim is to connect the groups which will be in the institute beyond my retirement and to help the others find attractive positions outside. Consequently the insoluble monolayer work (Brezesinski) also takes into account enzymes at interfaces and the wetting and crystallization work (Riegler) will develop closer interactions with theory. It is, however, not yet clear if and how the Miller group will develop their internal cooperations. The latter could result if amphiphilic carbohydrates can be purified sufficiently for interfacial studies.

The work on self-repairing coatings (Shchukin) has received much attention and also funding (see below), but this is at the moment concentrated on corrosion protection. Yet the key issue is to use a stimuli responsive release in a feedback-loop as often found in nature, e.g. to regulate pH, concentration of ions, enzymes, drugs, temperature or potential. Most obvious other technical applications could be anti-friction or anti-fungal coatings, but one may envision even more sophisticated regulatory circuits. The work on remote release (Skirtach) is now encountering strong competition, and there will be a heavy effort and excellent collaborations needed to maintain the lead. The issue here is to define and to develop the most important topics in cell biology and immunology.

The activities on sonochemistry at surfaces concern important problems involving the interfaces solid/ liquid, liquid/ gas and solid/ gas and I would like to drive these activities towards the beginning of the process, where gas bubbles are nucleated at a surface, and for these in situ-studies will be set up.

My own role will predominantly be (and has been) to most actively support those groups which will be terminated in the next 2-3 years. In addition I will collaborate with postdocs not belonging to any group but doing work I find worth supporting. This concerns new postdocs coming with a stipend or from collaborating groups, working in a sandwich programme. I will also assemble a group of postdocs working on different aspects of sonochemistry with the intention to become one of the leaders internationally in this field.

One major recognition has been a highly competitive (6 winners out of 142) and large (1.9 Mio Euro/ 2 years) grant to *D.G. Shchukin* in a new programme of the ministry of education and technology on "Intelligent Nanocontainers for Self-Repairing Coatings". The aim here, however, is to develop an application that can be the base of a start-up company. This is beyond the institute's mission and therefore this project is located in the neighbouring technology center GOIN. Still I will very much support it, because it would be great and a new experience to develop a process of "immediate" use.

Further recognition has been the Wolfgang-Ostwald medal I received 2009 from the Kolloid-Gesellschaft and the BP visiting lectureship 2010 I received from Cambridge University. I have also supported applications of our co-worker D.V. Volodkin who won the ERC starting grant and the Sofia Kovaleskaja award. With these awards he will continue his research at the neighbouring Fraunhofer institute for biomedical technology which, in view of our present space limitation provides the better environment for the project.

As mentioned before the department of interfaces will persist another 2-3 years, 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 5 departments and there is consensus that this should focus in a broad sense on physical chemistry. If they are successful this then would enable an easy transfer of scientific and technical staff into this department. 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. Therefore those remaining do not feel to be on a sinking boat but on a ship with high speed, helping them to find proper directions. I hope this process can be continued in a harmonic way, because these people have very well served science, but above all science should serve people.

Helmuth Möhwald
Director of the Department of Interfaces

Langmuir Monolayers as Model Systems to Study Interactions at Interfaces

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1974: Diploma, Biophysics
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Thesis: The parametric pump – a physical-chemical model of the active transport of ions in cells
1981: PhD, Physical Chemistry
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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)

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Aims

During the last years, the main aim of our research was the determination of structure/function relations for proteins and peptides. Their interactions with selected lipids in 2D and 3D model systems have been investigated. The work with enzymes at interfaces **[1]** has been interrupted to restart it with new questions and collaborations. The investigation of beta-sheet forming peptides (cooperation with B. Koksch, FU Berlin) **[2, 3]** as well as of antimicrobial peptides (cooperation with J. Andrä, Research Center Borstel) is ongoing **[4]**. The study of non-viral transfection systems (cooperation with B. Dobner, University of Halle) is also ongoing **[5-7]**. In this report, the main results of our work with the amyloid-β peptide(1-42) **[8-10]** and the interfacial behavior of polymer capped Fe_3O_4 nanoparticles **[11-12]** will be described.

Selected Achievements

Controlling Amyloid-β Peptide(1-42) Conformation by Nanoparticles

The amyloid-β peptide (Aβ) is a major fibrillar component of neuritic plaques in Alzheimer's disease brains and is related to the pathogenesis of the disease. Soluble oligomers that precede fibril formation have been proposed as the main neurotoxic species contributing to neurodegeneration and dementia. We hypothesize that oligomerization and cytotoxicity can be repressed by nanoparticles (NPs) that induce conformational changes on Aβ42 (cooperation with the Department of Chemical Engineering, University of Porto, Portugal, and the Institute of Molecular and Cellular Biology, Porto, Portugal). Fluorinated NPs, which promote an increase in α-helical content, exert an anti-oligomeric effect whereas hydrogenated analogues do not, leading to aggregation. Cytotoxicity assays showed that the conformational conversion of Aβ42 into an α-helical enriched secondary structure has also antiapoptotic activity, increasing the viability of cells treated with oligomeric species. Additionally, NPs were synthesized by sulfonation and sulfation of polystyrene (cooperation with Dr. Klaus Tauer, Colloid Chemistry Department), leading to microgels and latexes. Both polymeric nanostructures affect the conformation of A inducing an unordered state. Oligomerization was delayed and cytotoxicity reduced (**Fig. 1**). The proper balance between hydrophilic moieties and hydrophobic chains seems to be an essential feature of effective NPs.

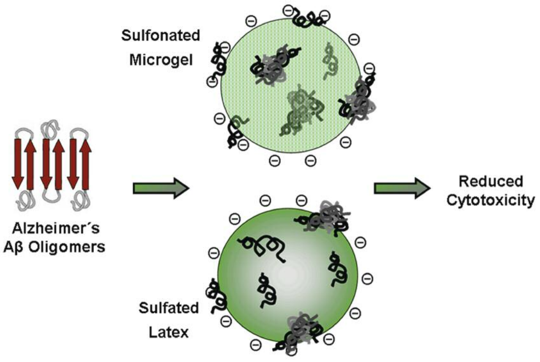

Fig. 1: Sulfonated and sulfated polystyrene NPs interact with Aβ peptide inducing randomization of its structure. As a consequence, the oligomerization process is disturbed and the peptide induced toxicity to neuroblastoma cells is reduced. These results comprise attractive achievements for the development of approaches for the study and therapy of protein misfolding diseases.

Polymer Capped Fe_3O_4 Nanoparticles at the Air/Water Interface

The interfacial properties of Fe_3O_4@MEO_2MA_{90}-co-$OEGMA_{10}$ NPs, recently developed and described as promising nanotools for biomedical applications, have been investigated at the air/water interface (cooperation with Dr. Dayang Wang, Interface Department). These NPs don't behave as classical amphiphiles. Once adsorbed at the air/water interface, they do not exchange with NPs in bulk, but they are trapped at the interface. This means that all NPs from the bulk adsorb to the interface until reaching a maximum coverage of the interface which corresponds to values between $6 \cdot 10^{-4}$ to $8 \cdot 10^{-4}$ mg/cm^2 and a critical equilibrium surface tension of ~47 mN/m. By using a special one barrier Langmuir trough equipped with two surface pressure microbalances, we have shown that the NPs are squeezed out from the interface into the aqueous subphase, and they re-adsorb on the other side of the barrier (**Fig. 2**). The results have been supported by TEM as well as AFM experiments of transferred Langmuir-Schaefer films on solid supports (**Fig. 3**).

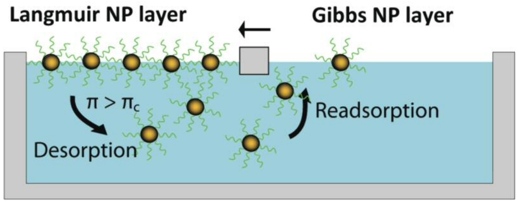

Fig. 2: Schematic representation of the desorption / re-adsorption of the Fe_3O_4@MEO_2MA_{90}-co-$OEGMA_{10}$ NPs from / at the air/water interface

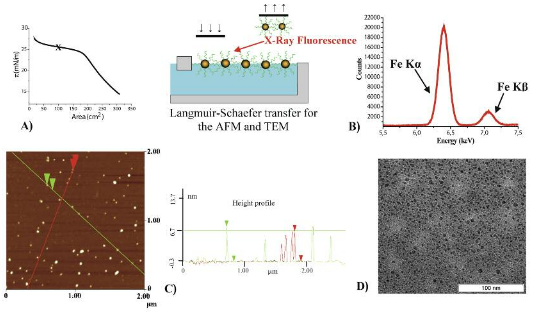

Fig. 3: A) Schematic representation of the NP layer at the air/water interface. The X mark on the compression isotherm (at 25 mN/m) shows the state where the film was investigated by TRXF, AFM and TEM; B) X-ray fluorescence showing the Fe Kα and Fe Kβ peaks C) AFM and D) TEM images of the NP Langmuir layer transferred on mica or on a copper grid, respectively, by the Langmuir-Schaefer technique.

The critical interfacial area of the Fe_3O_4@MEO_2MA NPs at the air/water interface above the LCST (lower critical solution temperature) is only 13% smaller than that below the LCST. More surprisingly, the NP layers proved to be very similar before reaching the critical surface pressure, independent of the subphase type (water or 1M NaCl) or temperature (below or above the LCST), as assessed from compression isotherms, IRRA spectra, and electron density profiles. In this state, the NPs adsorb at the interface in the pancake-like conformation, forming a densely packed layer. In contrast, above the critical surface pressure, the Langmuir NP layers exhibit different features below and above the LCST. Thus, on the plateau region, below the LCST, the pancake-like structure co-exists with the more hydrated brush-like conformation. Therefore, above the LCST, the weakly hydrated copolymer shell induces the accumulation and agglomeration of the NPs at the interface, allowing the formation of a well packed homogeneous monolayer of NPs. To summarize, the present work reveals that the Fe_3O_4@MEO_2MA NPs behave oppositely at the air/water interface below and above the LCST due to conformational changes of the copolymer chains. These changes occur upon variation of the temperature or the ionic strength of the aqueous subphase and only as a consequence of lateral compression of the film to surface pressures above the characteristic critical surface pressure of the NP layer (**Fig. 4**).

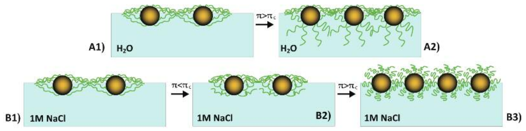

Fig. 4: Schematic representation of the interfacial behaviour of the Fe_3O_4@MEO_2MA NPs dictated by the conformational changes of the copolymer: A) below the LCST, the pancake-like configuration co-exists upon lateral compression with the brush conformation; B) above the LCST, the mushroom-like structure is induced by lateral compression of the NP film existing in a pancake conformation.

Future Plans

1. To study the interaction of peptides with biological membranes is one of the most challenging problems in biophysical chemistry. We will continue our cooperation with the Research Center Borstel to study systematically antimicrobial peptides using mono- and bilayer systems aiming to answer the following questions: (1) How does the membrane environment influence peptide/protein folding, (2) What is the influence of the peptide on the model membrane structure, and (3) Derive a model for the mode of action of these peptides.

We will continue our successful collaboration with the Koksch group at the Free University of Berlin to investigate model peptides which are involved in neurodegenerative diseases. The study of the influence of lipids and ions (Cu and Zn) on the folding behavior in bulk and at the interface using different methods is ongoing.

2. The study of non-viral transfection systems will be continued and extended by a new cooperation with the Santer group from Potsdam University. We will additionally link our experimental results with theoretical models (cooperation with K. Bohinc, Slovenia).

3. Chemically modified phosphoinositides will be studied in pure and mixed systems in cooperation with the Department of Biomolecular Systems.These studies are performed with the vision to study enzymatic interactions involving these lipids.

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(QUASI) PLANAR INTERFACES – FLUID INTERFACES

Interrelation between Adsorbed Interfacial Layers and Free Foam Films Stabilized by Proteins and Surfactants

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1977: Research Stay
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Thesis: Adsorption kinetics and
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at liquid interfaces
1988: Habilitation, Physical Chemistry
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Thesis: Modelling of surfactants,
surfactant mixtures and macro-
molecules at liquid interfaces
1990/91: NCERC Fellow
(University of Toronto with
A.W. Neumann)
Since 1992: Group Leader
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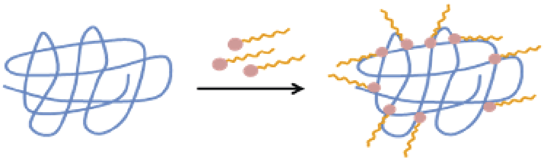
The main target of the group's activities comprises experimental and theoretical work on the thermodynamics and non-equilibrium properties of mixed protein-surfactant interfacial layers at water-air and water-oil interfaces. Work is under way to specify interfacial properties which correlate with the key parameters of corresponding foam and emulsion films, in particular their type, thickness and stability. The consequent question is whether the behaviour of foams and emulsions can be understood from the knowledge of the main properties of the corresponding adsorption layers and free films.

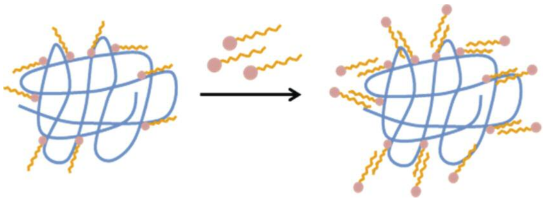
During the last five years we have been working intensively on various mixed protein-surfactant systems with the aim of understanding if and how adsorbed proteins can be replaced from the interface by surfactants, or prevented from adsorption by addition of surfactant to the solution, despite their much larger energy of adsorption as compared to typical surfactant molecules.

Mixtures of the globular protein lysozyme with different surfactants were studied in the PhD thesis of Veneta Alahverdjieva (2008), while in the PhD thesis of Csaba Kotsmar (2009) the random coil protein β-casein was studied in presence of ionic and non-ionic surfactants **[1-3]**. The investigations of the Humboldt fellow Vincent Pradines (2008/2009) were dedicated to the globular protein β-lactoglobulin in mixtures with ionic surfactants **[4]**. The continuation of this work at the water-air interface and different water-oil interfaces (hexane, triglycerides of different origin) is still going on. In conclusion of these studies we are able to draw the following picture. The addition of non-ionic surfactants leads to a hydrophilization of the protein, via hydrophobic interactions, which results in a step-wise decrease in surface activity of the protein-surfactant complex, as compared to the original protein molecules. Pre-adsorbed proteins can be replaced from the interface due to the same mechanism.



Scheme 1: Schematic representation of the formation of the hydrophobic protein-surfactant complexes showing electrostatic interaction between the protein and the ionic surfactant molecules

In contrast, the addition of ionic surfactants leads first to an increase in hydrophobicity (via electrostatic interaction) and thereby to an increased surface activity of the resulting protein-surfactant complex as compared to the original protein. Depending on the added surfactant, even precipitation of aggregates can be observed. With a further increasing surfactant concentration, a hydrophobic interaction sets in and leads to a further hydrophilisation of the protein-surfactant complex and consequently to a picture equivalent to that observed for non-ionic surfactants appears.



Scheme 2: Schematic representation of the increasing hydrophilization of the protein-surfactant complex via hydrophobic interactions between the surfactants' chains and the neutral complex

The orogenic displacement, discussed in literature as a possible mechanism for the displacement of proteins from interfaces by surfactants seems too simplified, as surfactants do not only compete with adsorbed proteins, they simultaneously modify the macromolecules' properties. The resulting complexes then become less surface active and can consequently be displaced from the liquid interface by competition.

As example of the replacement of a protein by a non-ionic surfactant, experimental data are shown below for the system β-casein with added amounts of dodecyl dimethyl phosphine oxide (C_{12}DMPO). **Fig. 1** shows the surface tension isotherm of the surfactant alone and of the mixtures with a fixed amount of protein (10^{-6} mol/l β-casein).

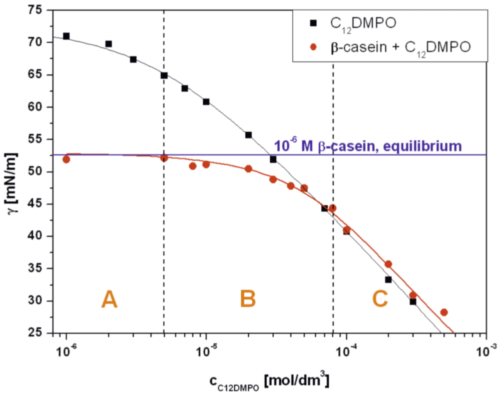


Fig. 1. Adsorption isotherm of a mixed adsorption layer at a fixed amount of 10^{-6} mol/l β-casein and increasing concentrations of the non-ionic surfactant C_{12}DMPO, the red and black lines were calculated from the thermodynamic model for protein/surfactant mixtures and the surfactant alone, respectively; data taken from ***[1]***

In **Fig. 2** the thicknesses of foam films stabilized with the same protein-surfactant mixtures are shown. The marked regions A, B, and C in **Figs. 1** and **2** correspond directly with each other.

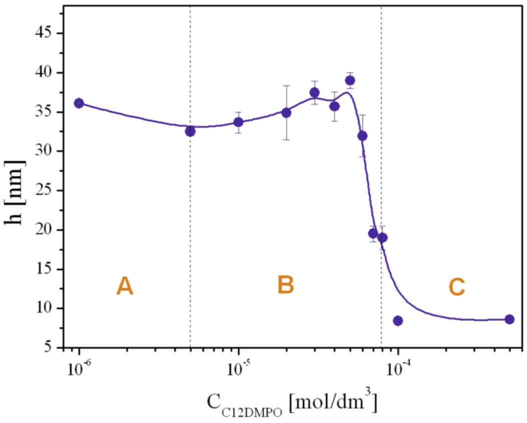


Fig. 2. Foam film layer thickness h of a mixed adsorption layer at a fixed amount of 10^6 mol/l β-casein and increasing concentrations of the non-ionic surfactant C_{12}DMPO; region A: mainly formed by the protein, region B: mixed layer; region C: transition to a pure surfactant layer; the curve is guide for the eye; data taken from ***[1]***

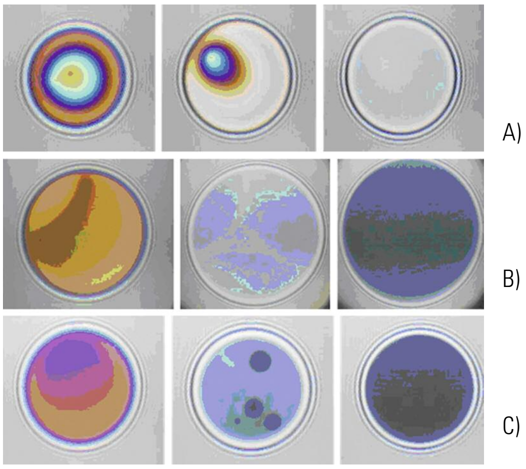


Fig. 3. Images of foam films corresponding to different states of the stabilizing mixed adsorption layers (the corresponding isotherm is given in Fig. 1 and film thickness given in Fig. 2) at a fixed amount of 10^6 mol/l β-casein;
A) 10^5 mol/l C_{12}DMPO; B) 8×10^5 mol/l C_{12}DMPO;
C) 5×10^4 mol/l C_{12}DMPO; images taken from ***[1]***

While in region A, the surface layer is essentially covered by proteins and highly surface active protein-surfactant complexes, in region B the surface layers are increasingly covered by free surfactant molecules, competing with complexes of less and less surface activity. Finally, in region C the surface layer and the foam films are mainly controlled by adsorbed non-ionic surfactant molecules.

This is supported by the measured film thickness (micro-interferometry), as shown visually in **Figs. 3**. In region A (graphs 3A) the thick grey equilibrium film has a thickness of 34 nm, which corresponds to about the thickness of a film stabilized by proteins. In region B (graphs 3B) we observe dark grey films with an ultimate thickness of 18 nm, a value that still allows incorporation of a few protein molecules. Consequently, in region C we can observe Newton black films with a thickness of 8 nm, which correspond mainly to surfactant foam films and their thickness does not allow to have a significant amount of protein molecules included.

The results obtained from dilational and shear rheology were in very good agreement with the observed behaviour of adsorption layers and foam films and support the general picture on the composition of the mixed adsorption layers **[2]**.

A special design for producing drops and changing the internal liquid inside a drop was used to demonstrate directly the displacement of proteins by sequentially injected surfactants **[5]**. This methodology has great potential also for other mixed systems and will be further explored.

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SOLID INTERFACES

Phase Transitions and Transport Phenomena in Thin Films at Solid/Air Interfaces

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Thesis: Light-induced drift of CHF3
1986: PhD, Physics
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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,
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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.

There is great scientific and technological interest in small, confined systems, ranging from molecularly thin films, molecular clusters, nano-particles, nano-rods, etc., to biological systems. Even bulk systems are affected by confinement effects. For instance, first order phase transitions begin with nucleation, a process dominated by confinement/interfacial effects. Also, many solid bulk materials are not homogeneous. Their properties are affected by their internal nanoscopic or microscopic structure. Hence, investigating phase transition and transport phenomena under confinement is of scientific and technological relevance.

Work:

We investigate the following specific topics/questions:

1.) *How do nanoscopic interfacial morphologies and line tension affect nucleation and growth of small aggregates?*
2.) *How does a surrounding interface affect the solid/liquid phase transition behavior of adsorbed liquid films?*
3.) *How do nanoscopic steps (rims) affect the solid/liquid phase transition behavior of adsorbed films?*
4.) *How do interfacial properties affect the coalescence behavior of sessile droplets of completely miscible liquids?*
5.) *How can nucleation and self-organized cluster growth be used to prepare/optimize organic photovoltaic cells?*

1.) Local interfacial properties (roughness, chemical composition, etc.) influence the heterogeneous nucleation and growth of small aggregates at surfaces. This is well accepted, but quantitative experimental studies are virtually non-existing. We investigate by AFM the impact of artificial, nanometer size morphological surface modifications on the nucleation and growth of fullerene (C60) aggregates from supersaturated solutions (**Fig. 1a**). We also measured the line tension τ ($\approx$-10^{-11}N) of sessile C60 droplets/aggregates (**Fig. 1b**) that transform with increasing volume - because of the negative τ - from 2-dimensional domains into sessile droplets.

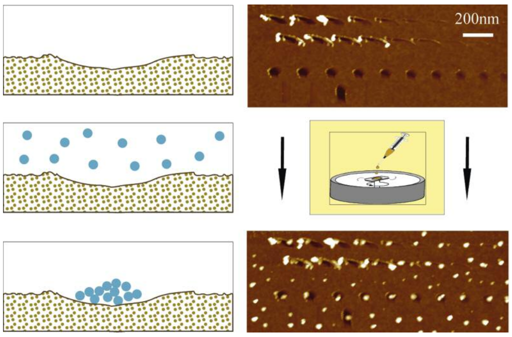

Fig. 1a: Influence of indentations in SiO_2 surfaces (depth <2nm!) on the location and growth of C60 aggregates.

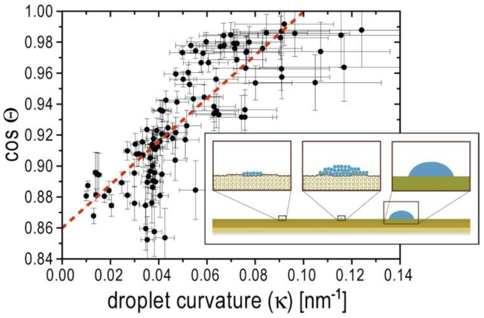

Fig. 1b: Contact angle as function of the curvature of the surface contact area (α inverse of droplet size) of C60 aggregates on SiO_2. The cartoon shows the variation of the aggregate shape with increasing volume.

2.) The wetting properties of surrounding interfaces broaden the (first-order) solid/liquid phase transition of adsorbed aggregates through interface-induced pre-melting. This phenomenon is used as a general tool to quantify the intermolecular interactions within adsorbed sub-monolayer films (**Fig. 2a**).

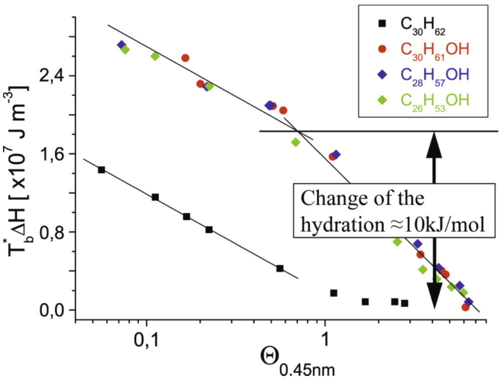

Fig. 2a: Lateral molecular interactions in alkane and alcohol submonolayers as function of the coverage. Below 1$\Theta_{0.45nm}$ (= 0.45nm average coverage) both substances show the same 2-d gas behavior (identical slopes). Above, the alcohol interactions are dominated by changes in the hydration as function of the coverage.

3.) Molecularly thin solid monolayer terraces of long chain alkanes melt with the appearance of (moving) liquid alkane drops at the terrace edges (liquid alkane wets neither its own solid nor the substrate). Amazingly, the drops (**Fig. 3a**) are magnitudes larger than the terrace height. A "text-book" melting/nucleation scenario does not explain this finding because it predicts a continuously growing, stable liquid channel at the terrace edge as the temperature rises (I → III, **Fig. 3b**). Eventually the *entire* channel disconnects at the terrace edge and rapidly melts "into" the solid. Instead, we postulate the fluctuation-driven formation of liquid bulges/drops (**Fig. 3b**, IV) *before* the entire channel becomes unstable. This explains the observed large drop sizes. More important, we introduce a new nucleation pathway via a morphological transition. It has a lower nucleation barrier and should be relevant for numerous ubiquitous systems (capillary condensation in scratches, etc).

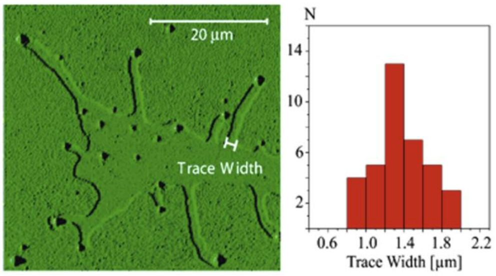

Fig. 3a: Surface partially covered with a solid alkane monolayer heated above melting and then rapidly cooled (→ fixed topology for AFM, trace width at the terrace edge = original droplet size).

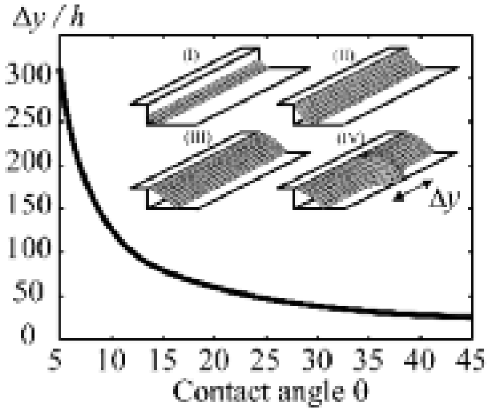

Fig. 3b: Channel morphologies at the terrace edge and bulge size $\Delta\gamma$ normalized to h as function of Θ.

4.) Recently we found that sessile drops of completely miscible liquids often do *not* coalesce rapidly upon contact. Unexpectedly (capillary pressure promotes rapid coalescence), they remain separated but connected via a thin liquid film (**Fig. 4a**). As cause for this "delayed coalescence" we identified the surface flow between the two drops due to the different surface energies $\Delta\gamma$ (**Fig. 4b**). This flow results from a subtle balance between convectional and diffusional components leading to fast and delayed drop fusion depending on the contact angle(s) and surface energies.

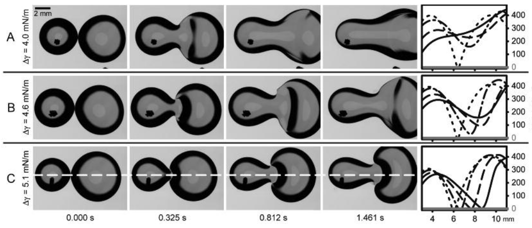

Fig. 4a: Time sequences of sessile drops on SiO_2 surfaces (top view). Rows A, B and C: various 1,2-butanediol/water mixtures (various $\Delta\gamma$) with fast (A) and delayed coalescence (B, C). Drop height profiles derived along the white line (C).

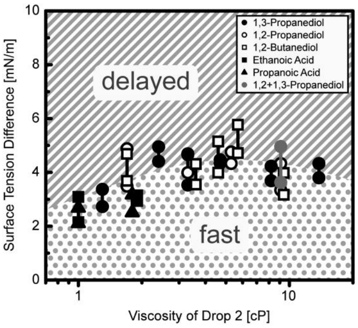

Fig. 4b: Phase diagram of the coalescence behavior: Surface tension difference $\Delta\gamma$ vs. viscosity ($\Theta \approx 10^0$). $\Delta\gamma$ >2-4mN/m leads to delayed coalescence.

5.) Heterojunction organic photovoltaic cells need nanometer size structures of the donor/acceptor system to avoid exciton recombination prior to charge separation. We use nucleation and self-organized growth to achieve and optimize suitable donor/acceptor structures (**Fig. 5a**).

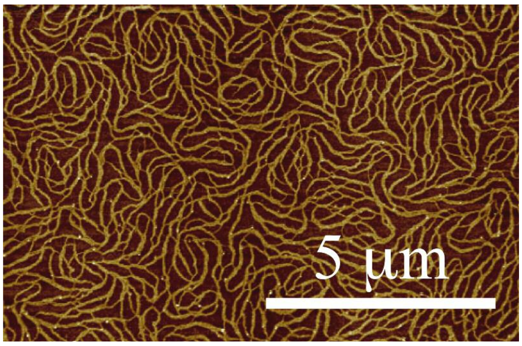

Fig. 5a: Self-organized structures (AFM, dip-coating → drying patterns) of Cu-Phtalocyanine on a SiO_2 surface. The structures are only 1nm high.

Future Plans:

We will proceed investigating heterogeneous nucleation and the growth of (small) aggregates. We will prepare nanometer size, defined "active sites" (indentations, etc.) on planar solid surfaces and investigate (AFM) their impact on the adsorption, nucleation and growth of aggregates from supersaturated solutions. Future experimental and theoretical work on the phase transition behavior of molecularly thin alkane terraces will also address nucleation and growth phenomena, but within solid/liquid phase transitions. Molten alkanes do not wet their own solid - a unique property. Thus the studies will also focus on melting in general. We will go on using nucleation and self organized pattern growth for the preparation of organic photovoltaic hetero-junction cells. This work aims at a better understanding of the physics of typical wet preparation processes (spray-, spin-, dip-coating). The resulting (drying) structures are influenced by (surface) flow and solvent evaporation, phenomena that will be studied in detail by future drop coalescence experiments.

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How capillary instabilities affect nucleation processes.
Physical Review Letters, in revision.

NON-PLANAR INTERFACES

Joint French-German Laboratory (LEA) on Sonochemistry

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1974: PhD, Physics (University Göttingen, Max-Planck-Institut für Biophysikalische Chemie, A. Weller, E. Sackmann)
Thesis: Lokalisierte und delokalisierte Triplettzustände in Einkristallen von Elektron-Donor-Akzeptor-Komplexen: ESR- und emissionsspektroskopische Untersuchungen zwischen 4K und 300K
1974-1975: Postdoc (IBM San Jose)
1975: Research Assistant (University of Ulm)
1978: Habilitation, Physics (University of Ulm) Thesis: Transporteigenschaften und Phasenübergänge in organischen Charge-Transfer Kristallen
1978-1981: Scientific Coworker (Dornier-System, Friedrichshafen)
1981: Associate Professor C3, Experimental Physics (TU München)
1987: Chair C4, Physical Chemistry, (University of Mainz)
Since 1993: Director and Scientific Member (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 1995: Professor, Physics and Physical Chemistry (University Potsdam)
Since 2001: Honorary Professor (Zheijang University, Hangzhou)
Since 2004: Honorary Professor (Fudan University, Shanghai)
Since 2006: Honorary Professor (Institute of Chemistry at the Chinese Academy of Sciences, Beijing)

General and Aims

The joint laboratory was established in 2008 with the Institute of Separation Chemistry (ICSM) in Marcoule which is co-sponsored by CEA, CNRS, Univ. Montepllier and Ecole de Chemie at Montpellier. Since the laboratories in Marcoule were ready for use only in 2009 work started with French guests in addition to MPI scientists in Golm and now proceeds at both laboratories via frequent exchange of scientists.

Common goal of the laboratory is understanding and controlling the mechanism governing sonochemical reactions. These reactions are very promising as they result from the collapse of ultrasonically produced cavitation bubbles which for short time (< µsec) and locally (< 10µm) produce high temperatures (~10^4 K) and pressures (1000 atm). In order to arrive at understanding several different lines of experiments have been set-up.

1. A single bubble sonoluminescence measurement has been set up to study temperatures and reactive species involved in the process. A comparative multibubble experiment is set up at Marcoule.
2. The sketch of bubbles at different surfaces (**Fig. 1**) shows that many interfaces are involved **[1]**. Consequently the influence of surfactants and surfaces on the sonochemical reaction should be studied.

In order to apply the method one may envision various processes, some of them will be studied in the LEA.

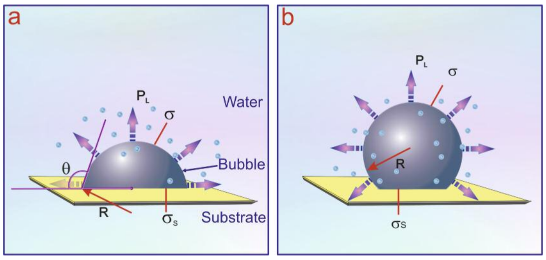

Fig. 1: Scheme of a bubble of radius R on a hydrophobic (a) and a hydrophilic (b) surface with solid surface energy σ_S liquid surface energy σ_L and contact angle Θ. The bubble grows because of a pressure difference P'- P_L between inside and outside.

3. Nanoparticles of non equilibrium shape and composition should be prepared and arranged. This topic has been addressed in the contribution by D.G.Shchukin.
4. The process may be used to separate ions by either selective leaching of a solid or by flotation. This is a long term goal of ICSM concerning actinides, but is also of more general interest in e.g. analytical and environmental chemistry.

Results

Ad 1: The single bubble luminescence spectra showed very interesting and promising results. **[2]** The spectra can be deconvoluted into a continuum akin to black body radiation of a plasma and into narrow emission of reactive species like OH^* and Na^* (**Fig. 2**). Surprisingly (and not understood) the broad emission is observable in only a narrow range of acoustic pressure (± 10%), and at a higher pressure the line emission steeply increases (**Fig. 3**). It is also remarkable that the Na line is observed preferably in the presence of sodium dodecyl sulphate. Apparently the detergent enriched at the bubble surface attracts enough Na^+ that later is excited during the bubble collapse. In the specific case of OH emission the single and the multibubble emission spectra agree.

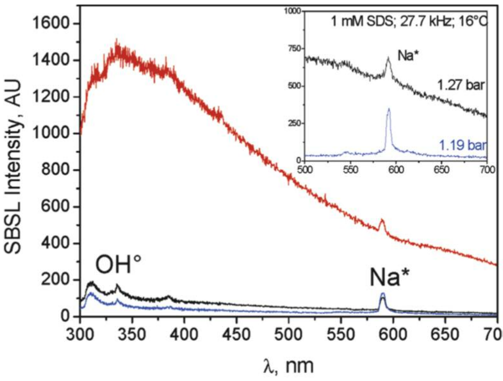

Fig. 2: Sonoluminescence spectra (28 kHz) of a 0.5M NaCl solution regassed with 70mbar Ar at acoustic pressures of 1.25 (red), 1.20 (black) and 1.15 (blue) bar. The inset shows the spectra after addition of 1mM SDS at two different acoustic pressures (indicated) [2]

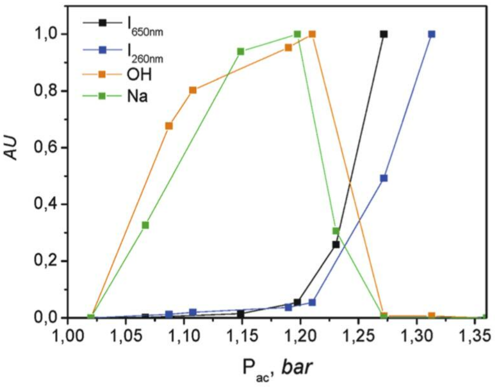

Fig. 3: Dependence of the sonoluminescence intensity on acoustic pressure P_{ac} for wavelengths corresponding to the broad emission (650nm, 260 nm) and for the lines ascribed to Ar and Na. [2]

Ad 2: Creating patterns of hydrophobic and hydrophilic areas on a surface we can show that, at least for a soft surface, cavitation occurs predominantly on the hydrophobic areas. /13/ This is in accordance with a developed nucleation and growth model for heterogeneous surfaces. Metallic films evaporated on silica or glass present an especially interesting system since the surface can be made atomically flat and transparent to enable application of evanescent optical techniques. In these cases ultrasound may introduce vey specific patterns of dewetting of the film from the surface (**Fig. 4**).

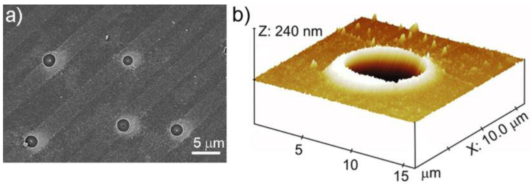

Fig. 4: (a) SEM image of a 100nm Al film on a micropatterned silicon wafer with the hydrophobic areas more bright after 10 min of ultrasonic treatment (20 kHz, 51.3 W/cm^2). b) AFM image of one of the spots on the left.

Ad 4: Ultrasonic activity on a hard surface like glass differs very much from that on the soft Al. Here one clearly recognizes that it starts on micron sized defects (**Fig. 5**). **[4]** Therefore the fraction of eroded area increases nonlinearly with sonication time. This nonlinearity holds also for leaching, and in the specific case it was shown that it is very selective. Here the Al/Na ratio in solution increases by more than an order of magnitude with sonication time increase from 20 minutes to 1 hour (**Fig. 6**).

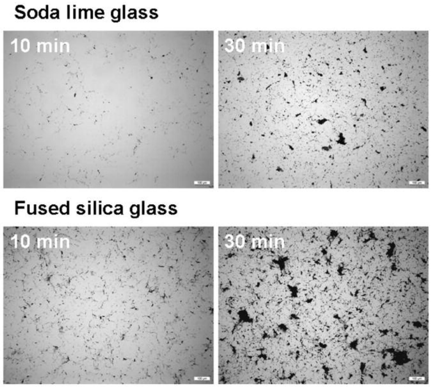

Fig. 5: Optical micrographs of two different glasses after 10' and after 30' ultrasonic treatment. [4]

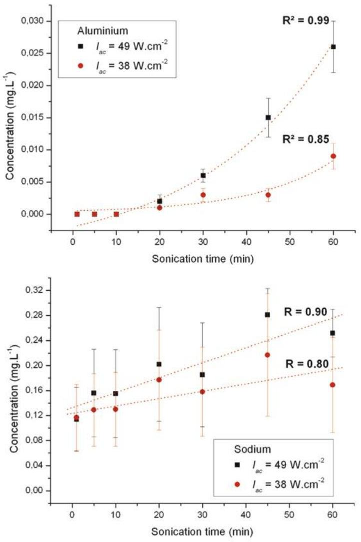

Fig. 6: Ionic concentration of Al (top) and Na (bottom) in solution as a function of sonication time for different intensities (indicated) [4]

Another way of ion separation is by flotation where gas bubbles are made with much surface for ion binding. Ultrasound is a very clean, controlled and fast method of preparing these bubbles. **[5]** This way one makes use of ion specific binding to an ionic or in this case a non-ionic polyoxyethylene surfactant at the interface. We could show that the ion specificity follows the Hofmeister series. The data obtained on ion extraction were sufficiently quantitative to derive thermodynamic data (**Fig. 7**) These indicate a dominant contribution of dehydration energies upon ion binding.

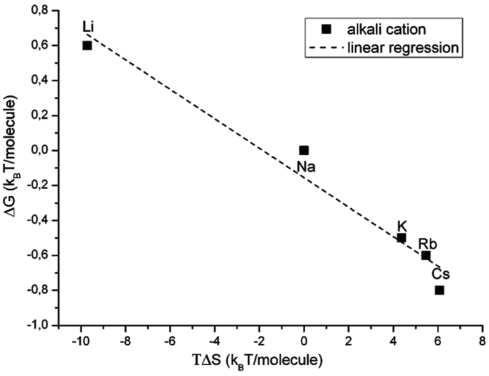

Fig. 7: Free energies of binding versus solvation entropy for different ions with Na$^+$ as reference [5].

Future Development

The work on sonochemistry within the LEA will be developing in different directions, mostly concentrating on solid surfaces.

- Understanding and controlling the process at surfaces laterally structured chemically and geometrically.
- In-situ analysis of the process by light scattering of evanescent waves and by sonoluminescence.
- Extension of single bubble luminescence studies towards higher spectral resolution to derive the local temperature of the emitting species.
- Work on properties of structured surfaces and foam films and nanoparticles will be pursued outside the LEA. Also work on ion separation will be pursued exclusively at Marcoule.

The first period of the LEA will end in December 2011, but an extension is planned. For this, however, the topic will be broadened beyond sonochemistry including also other departments. To prepare this the French partner Prof. T. Zemb will spend some months in the institute, as he won a Gay-Lussac Humboldt award.

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Active Interfaces and Coatings

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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 **[1-7]**. 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 (humidity, electromagnetic irradiation). The coatings could also have several functionalities.

The release properties and re-loading ability of polyelectrolyte-modified halloysite nanotubes, TiO$_2$ nanoparticles, and polyelectrolyte capsules were studied **[1-3, 5-7]**. All nanocontainers revealed an increase of the inhibitor (methylbenzothiazole, 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. A novel approach of local corrosion termination using UV-irradiation has been studied. The possibility of release of corrosion inhibitor and fluorescent dye from titania based polyelectrolyte containers under UV-irradiation was demonstrated. Use the porous containers allows loading the wide spectrum of chemicals inside the containers, thus this system consists of nanosized reservoirs. A polyelectrolyte shell, which modified the outer surface of the containers prevents the untimely release of the loaded material. Moreover, nanocontainers with titania core revealed an increase of the benzotriazole (corrosion inhibitor) release under UV-irradiation twice faster in comparison with pH stimulated release. Simultaneously, the highest release efficiency under pH change in the corrosion process was up to 65%, for titania-based mesoporous nanocontainers, however, if one uses the UV-irradiation the release could be increased up to 86%. Thus it should be noted that for the coatings where very fast and regulated release is necessary, the use of UV-irradiation is strongly preferable.

Halloysite aluminosilicate nanotubes with 15 nm lumen, 50 nm external diameter, and length of 800 ± 300 nm were developed as containers for loading, storage, and controlled release of anticorrosion agents and biocides **[6]**.

Mesoporous silica nanoparticles have been synthesised and tailored for dispersion into a solvent-borne polyester-based coating. When dip-coated onto steel, hybrid coatings comprising the primer impregnated with ≥ 1 wt% of these nanoparticles loaded with benzotriazole were found to present a strong passive layer, preventing corrosion in 1 mol dm^{-3} NaCl (**Fig. 1**). To obtain similar improved performance the required concentration of benzotriazole when added directly to the primer (without nanoparticles) was at minimum tenfold greater. On formation of artificial defects in the surface the hybrid coating displayed strong impedance to corrosion, several orders of magnitude greater than those seen previously in similar systems. The scratched hybrid coating incorporating 2 wt% nanoparticles was found to impede corrosion by almost as much as the intact primer.

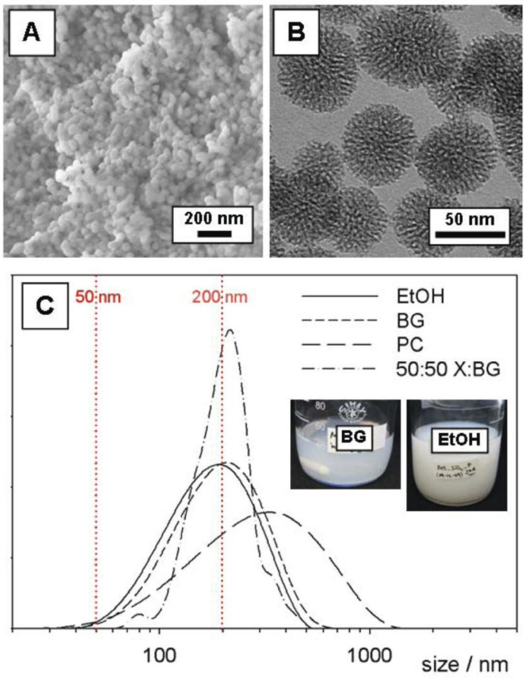

Fig. 1: A and B: SEM and TEM images of mesoporous silica nanoparticles (NPs). C: DLS profiles, and (inset) visual appearance of the NPs in different solvents of intermediate polarity. Key: EtOH = ethanol, BG = butyl glycol, PC = 1,2 propylene carbonate, X = xylene.

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 pro-

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vide unique means for forming nanomaterials with non-equilibrium structure under extreme conditions **[8-14]**. 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 **[8, 13]**. For the first time a novel method of formation of mesoporous metal sponges and surfaces by ultrasonic treatment was demonstrated in aqueous media both on the surface of metal plates and inside metal microparticles. Aluminum, titanium, nickel and magnesium exhibit a well-defined mesoporous nanostructure after sonication. An oxide layer forming very quickly in water can stabilize the structural changes caused by ultrasound irradiation. The novel method is universal and can be applied to a wide variety of metals with only one exception – noble metals are stable to ultrasonic treatment and do not form a porous sponge structure. The application of ultrasonic treatment of surfaces and bulk of the metals can open a lot of opportunities in different fields, for example, as thermoelements, catalysts, light materials, for metal protection. By patterning a surface one may verify models of heterogeneous nucleation of cavitation bubbles, and the following impact on surfaces was qualitatively as expected varying surface energies, temperature and ultrasonic powers (**Fig. 2**) **[15]**. One expects cavitation bubbles to grow towards diameters of 100 µm, and one may limit the contact area well below this studying also the pinning of the three phase line. This provides an additional control (or way of preparation) of surface treatment by ultrasound.

Stable monodisperse gold, silver, and gold-silver alloy nanoparticles with the variable average diameter of 5-30 nm were used for modification by ultrasound at room temperature **[9, 10,]**. The prepared gold nanoparticles were mixed with silver salt or silver nanoparticles and successively sonicated step by step. 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. More than 1 hour of ultrasonic irradiation is required to create gold-silver structures with shape and depending on surface active additive XRD and ED patterns of final samples proved the presence of polycrystalline or amorphous gold-silver nanoalloys or gold nanoparticles.

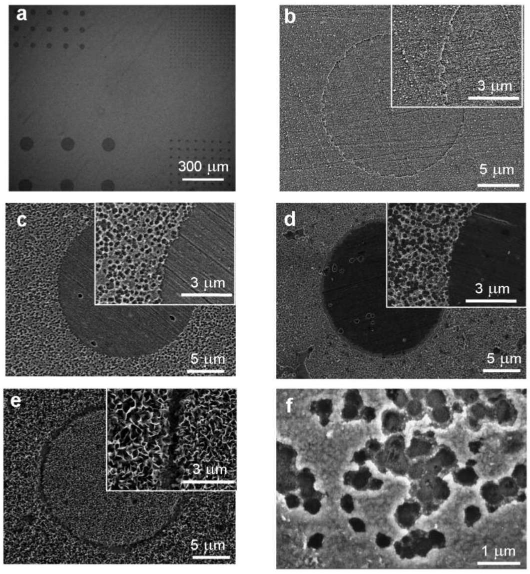

Fig. 2: SEM images of the patterned Al plate before ultrasonic treatment (a, b) and after ultrasonic treatment: (c) - at 10 min of sonication, (d) – at 30 min of sonication, (e) – at 40 min of sonication, (f) – high magnification of the hydrophobic surface with pits at 30 min of sonication. The inner circular area is hydrophilic; outer part is hydrophobic. Temperature of the treatment is 340 K.

A new protective coating for hydrogen storage materials was prepared by the Layer-by-Layer technique. Dichloromethane was used as the solvent for polyelectrolyte dissolution and Layer-by-Layer assembly of the polyelectrolyte shell. The sodium borohydride/polyelectrolyte composite is more stable compared to unprotected sodium borohydride during storing in open atmosphere. The polyelectrolyte shell protects water-sensitive metal hydrides against moisture and air. The demonstrated approach for hydride protection can find applications in hydrogen storage systems and could be used in hydrogen fuel cells. A second approach for protection of hydrogen enriched materials involves polystyrene shell co-precipitation. This shell provides a hydrophobic barrier for water diffusion into the container interior. The stability of sodium borohydride microcontainers is increased as compared to the unprotected material by 2.5 times during storage at 100 % humidity.

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Ordering of Functional Nanoparticles

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The objective of directing colloidal nanoparticles (NPs) to self-assembly into tailored architectures is not only to create advanced materials with physicochemical properties programmed at the nanometer scale, but also to experimentally model various association processes occurring at the microscopic level such as crystallization. To fulfill that, however, one must have NPs with defined size, shape, and surface chemistry and be able to manipulate various strong and weak interactions between NPs and those interactions of NPs with the surrounding media in a similar way that we do with ions, atoms, and molecules **[1]**. To address these issues, our research has focused on 1) development of facile and reproducible strategies to synthesize monodisperse NPs in terms of size, shape, and surface chemistry, especially anisotropic NPs with patchy surface chemistry, 2) engineering of the surface energy of NPs to mimic the interfacial behavior of amphiphilic molecules, and 3) study and manipulate the balance of various interactions exerted on NPs during self-assembly.

A. NP Synthesis

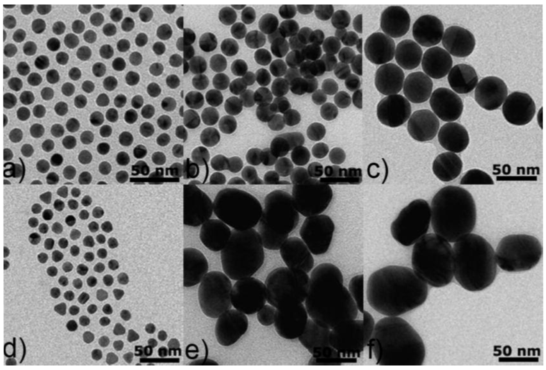

Fig. 1: TEM images of Au NPs obtained by the present method (a-c) and by the Turkevich method (d-f) at different citrate concentrations: 2.97×10^{-2} wt% (a,d), 1.01×10^{-2} wt % (b,e), and 6.10×10^{-3} wt% (c,f). The concentration of Ag+ ions in the present method was 8.5×10^{-6} wt%. The concentration of $HAuCl_4$ in both methods was 0.01 wt%.

Gold NPs can easily be produced and modified and their Plasmon resonance is highly sensitive to the interparticle spacing. So they are important building blocks to generate innovative materials with peculiar collective plasmonic properties and ideal models to monitor the spatial configuration of adjacent NPs over the course of self-assembly. Despite the fact that a number of methods have been developed to produce gold NPs in aqueous and organic media, citrate reduction of auric acid to gold NPs – Turkevich method invented 60 years ago – still remains the most flexible and feasible method to produce gold NPs with sizes spanning from 5 nm to 100 nm. The Turkevich method is very simple, namely, adding citrate to boiling aqueous solution of auric acid. However, the sizes of gold NPs obtained have a broader distribution and their shapes are rather irregular and non-uniform especially for large particles. This is due mainly to the pH buffer role of citrate that is usually less recognized but it must be taken into account as the activity of auric acid and the nucleation of gold NPs is strongly pH dependent. In order to temporally separate the buffer role of citrate from its reducing role and, at the same time, the nucleation of gold NPs from crystal growth, we have modified the traditional Turkevich protocol by adding a mixture of auric acid, citrate, and a trace amount of silver nitrate to boiling water. The new protocol allows formation of monodisperse, quasi-spherical gold NPs, whose sizes linearly increase from 12 to 36 nm with the decrease of citrate concentration (**Fig. 1**) **[2]**.

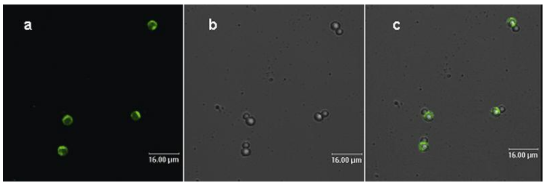

Fig.2: Fluorescence (a) and transmission (b) CLSM images of the anisotropic particles obtained by incubation of (PAH/PSS)3/FITC-PAH/PSS/PAH/PSS-coated 4.4 m PS particles in a THF/water mixture for 2 min, followed by redispersion in water with the means of centrifugation. (c) Overlay of the fluorescence and transmission CLSM images. The THF-to-water volume ratio is 1.5:1.

Anisotropic NPs with patchy surface functionalities provide better models for mimicking molecules. Synthesis of anisotropic NPs has accordingly been of both experimental and theoretical interest for decades. To produce truly Janus particles composed of chemically different constituent parts with different surface chemistry one usually implemented uses masks or masters as templates, but the template-assisted fabrication procedure has relatively low yield. By properly choosing the materials to achieve a better crystalline facet matching, one can directly synthesize a number of anisotropic Janus inorganic nanoparticles. Their surfaces are typically coated with the same ligands due to a one-pot synthesis procedure. We have recently successfully produced anisotropic polymer NPs with a snowman like shape via protrusion of the polystyrene (PS) cores from the polyelectrolyte multilayer (PEM) shells when PEM-coated PS NPs are incubated in water/THF mixtures and their surfaces are well separated into two distinct functional domains (**Fig. 2**) **[3]**. Our approach is rather simple and rapid (within minutes), and easy to scale up as compared with the methods reported in literature.

B. Interfacial Translocation of NPs

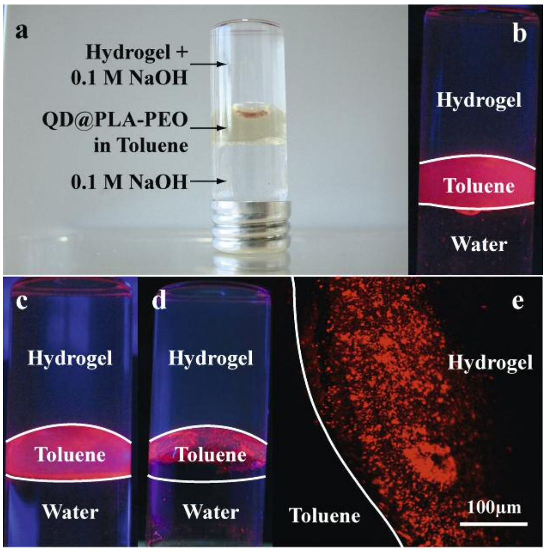

Fig. 3: CdSe@PLA/PEG NPs transfer from the organic phase to the aqueous phase in a triphasic system containing a NP toluene dispersion (the middle phase), a 0.1 M NaOH aqueous solution (the lower phase) and a hydrogel swollen by 0.1 M NaOH aqueous solution (the upper phase). The triphasic system was heated at 40°C. (a, b) Optical images of the initial triphasic systems recorded under sunlight (a) and by UV excitation (b). (c, d) Optical images of the triphasic system (c) and the hydrogel phase (d), washed by toluene and water several times to remove the excess of NPs, after 2 days of incubation at 40°C under gentle shaking. The images were recorded under UV illumination. (e) CLSM image of the cross section of the hydrogel phase, shown in Figure d, to determine the NPs penetration depth. Both the water/toluene interface and the hydrogel/toluene interface are highlighted by white lines.

Mimicking the interfacial behavior of surfactants will enable colloidal particles not only to self-assemble in diverse hierarchical liquid crystal structures embodied in surfactant self-assemblies, but also to monitor the mechanisms governing the changes in solvation for molecules crossing interfaces as well as to cross various biological barriers to accomplish diagnostic detection and therapeutic intervention. Recently, we have successfully directed hydrophobic colloidal NPs, coated with polylactide (PLA) and poly(ethylene glycol (PEG) to transfer from the organic to the aqueous phase across not only liquid/liquid but also gel/liquid interfaces after the PLA degradation (**Fig. 3**) **[4]**. Crossing the interface for NPs is exceedingly fast, and the transfer kinetics is limited by the NP diffusion in the bulk phases and the NP attachment at the interfaces. The NP transfer to the aqueous phase is hydrogen-bond selective.

C. Shape-Controlled Self-Assembly of NPs

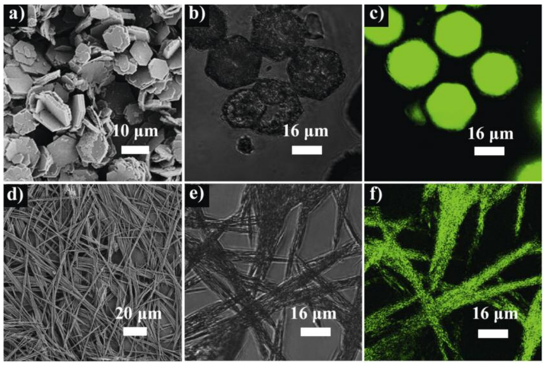

Fig.4 SEM (a and d) and CLSM transmission (b and e) and fluorescence (c and f) images of hexagonal flakes (a–c) and wires (d-f) obtained via controlled isotropic and anisotropic self-assembly of CdTe NPs stabilized by L-cystein.

NP self-assembly is dictated by the balance of various interactions between the NPs. Encouraged by our recent finding that electrostatic repulsion can act in an anisotropic fashion in the presence of dipolar interactions, we have meticulously manipulated the kinetics of self-assembly of negatively charged CdTe@L-cystein NPs by stepwise protonation of the carboxylic groups of the cystein coating and demonstrated a clear effect of the self-assembly kinetics on the self-assembly structures; the fast assembly causes anisotropic assembly structure while the slow assembly yields isotropic structures (**Fig. 4**). The transformation of anisotropic NP self-assemblies to isotropic self-assemblies with time has been also observed. This shape-controlled, electrostatic assembly of NPs not only leads to innovative materials – supercrystals – but also provides in-depth insight into agglomeration-based crystal growth, such as oriented attachment.

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Nanotechnology and Optical Manipulations of Capsules and Films

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The research group of nanotechnology and optical manipulation of capsules and films develops the methods of nanotechnology with application of electromagnetic fields for understanding processes relevant to biology and other fields. The aim is to advance in understanding of fundamental processes with potential linkage to practical applications. An important direction of research is devoted to development of spherical drug delivery vehicles and planar membranes with remote release capabilities for studying intracellular processes in the areas of immunology, protein science, etc. Nanoparticle self-assembly on spherical particles and planar surfaces as well as thermal processes at the nanoscale are also in focus. In addition, novel materials, for example carbon nanotubes and rare-earth elements are investigated.

The main goals of the group are:
- to understand intracellular transport of proteins and small peptides;
- to develop next generation of drug delivery vehicles for studying enzymatic reactions in models systems and in cells;
- to advance in the area of nano-manipulations;
- to investigate thermal properties of polymers and localized permeability control of membranes, films, polymers, etc.;
- to develop novel materials and membranes with built-in 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 intracellular release of SIINFEKL peptide inside a cell containing MHC (major histocompatibility complex) Class I molecules. The walls of the capsule are functionalized nanoparticle aggregates which absorb light energy and convert it to heat. These 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 near-IR laser light affects the permeability of the outer polymeric shell allowing materials to be released remotely. Intracellularly released peptides allow investigation of transport and cell surface presentation of proteins inside living cells – this area of research is of fundamental importance to immunology.

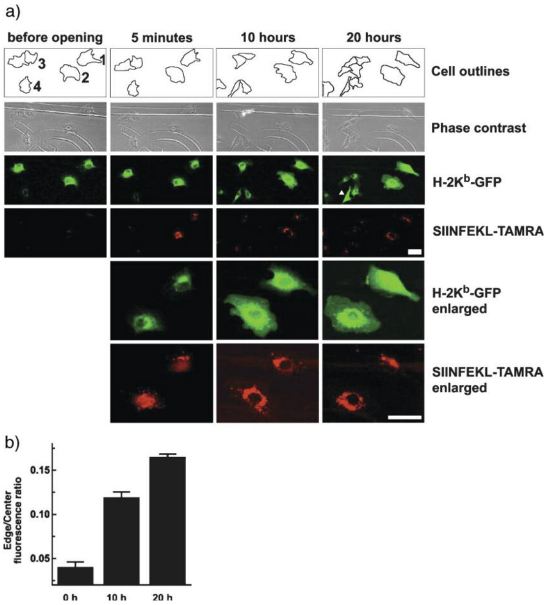

Fig. 1: Release of fluorescently labeled SIINFEKL peptide from the microcapsules leads to surface transport of H-2Kb–GFP without harmful side effects to the cells. a) Time course of capsule opening and class I transport. In cells 1 and 2 only, the microcapsules were opened at 0 min, and the TAMRA fluorescence spreads out into the cytoplasm (5 min). After10 h, a milky surface stain is visible in cells 1 and 2 but not in 3 and 4 (both of which divide during the time course). In one daughter cell of 4 (arrowhead),where the capsule is broken mechanically, leading to peptide release and surface transport of class I. The bottom panels show enlargements of cells 1 and 2. Scale bars are 50mm. b) Ratio of cell edge (surface) over cell center (total) fluorescence of H-2Kb–GFP at three time points (five cells from two independent experiments were analyzed; error bars show the standard error of the mean).

Next generation of intracellular and even in-vivo drug delivery carriers necessitates development involves more sophisticated structures. Several approaches to these novel and complex structures are under investigation. Microcapsules presented in **Fig. 2** depict several types of the so-called multicompartment microcapsules. These include concentric, pericentric, innercentric and acentric structures. Future investigation in this area is also devoted to designing anisotropic particles and capsules. Specifically, anisotropic multicompartment assemblies are of high interest.

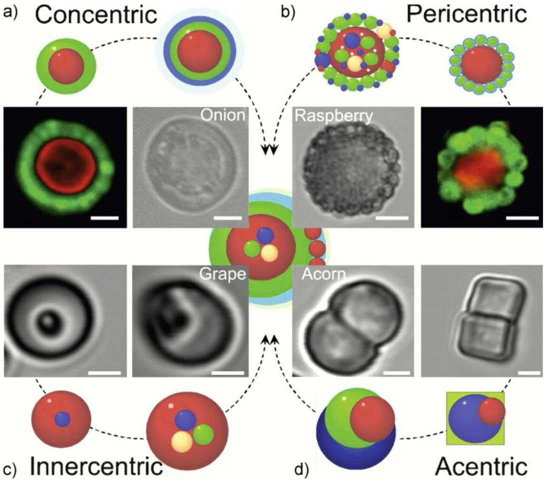

Fig. 2: Overview and the road-map for future directions of multicompartment microcapsules. Four different approaches are identified in the schematics: a) concentric, b) pericentric, c) innercentric, and d) acentric. The structure in the middle incorporates all four approaches. The corresponding confocal microscope images of the first steps in each direction are also presented. Scale bars correspond to 2 μm.

More advanced functionalities of drug delivery vehicles include direction-specific release. In case of giant microcapsules, which were used as a model system, direction-specific release can be accomplished by positioning of the laser beam, **Fig. 3** A very clear direction of release, which can be used for targeted delivery, can be clearly seen in this figure.

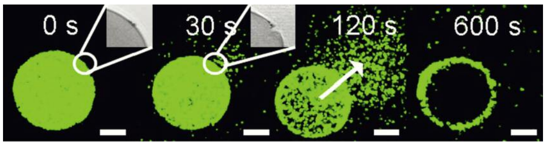

Fig. 3: Fluorescence microscopy snapshots of the site-specific opening of a giant polyelectrolyte capsule by IR laser activation. The inset shows the pore in the polyelectrolyte shell. The arrow indicates the direction of release as osmotic pressure drives encapsulated material out of the capsule.

The area of biocompatible films is very closely related to the main theme of drug delivery. Here functionalization by nanoparticles provides additional functionalities and may affect mechanical properties. **Fig. 4** demonstrates functionalization of films with gold nanoparticles. Both aggregated and non-aggregated states can be achieved. The latter allow biologically "friendly" near-IR light activation of the films.

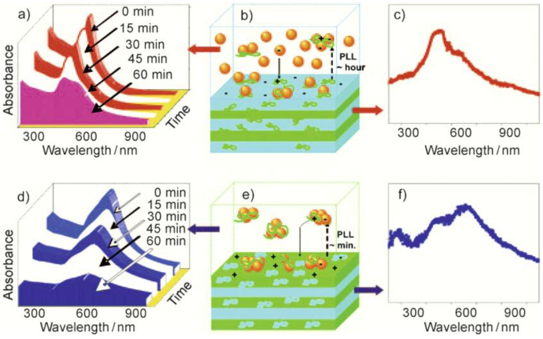

Fig. 4: Kinetics of adsorption of non-aggregated (a–c) and aggregated (d–f) nanoparticles onto biocompatible PLL/HA films. [Adsorption on (PLL/HA)24 films is shown in (a–c), while adsorption on (PLL/HA)24PLL films is demonstrated in (d–f)]. UV/Vis absorption spectra of the supernatant solution during adsorption in (a) and (d) were recorded at 15 min time intervals. Schematics of the interaction of nanoparticles and the films in non-aggregated and aggregated states are demonstrated in (b) and (e), and the corresponding UV/Vis absorption spectra of the films after nanoparticle adsorption are given in (c) and (f), respectively.

All areas of research rely on mechanically strong delivery vehicles, which, on the other hand, can be used as sensors of intracellular functions. This is reflected in future challenges and tasks.

Future Tasks:

- Investigation of intracellular transport properties relevant to immunology [with Jacobs University Bremen]
- Understanding mechanical properties of drug delivery vehicles for designed enhanced carriers and use them as intracellular sensors [with Bayreuth University, Bayreuth]
- 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
- Bio-compatible films [with Fraunhofer Institute of Biomedical Technology, Golm]
- Novel materials with optical and opto-electronic properties.

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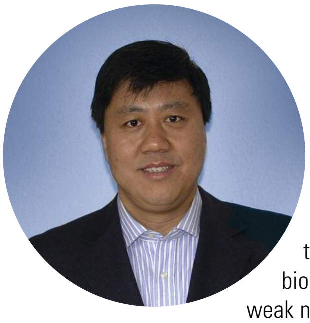
INTERNATIONAL JOINT LABORATORY

Molecular Assemblies of Biomimetic Systems and Nanostructured Design



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The “bottom-up” assembly of multifunctional biomimetic systems and bioinspired nanostructures at the molecular level is of tremendous interest because of the superior physical and biological properties of these materials in comparison with conventional synthetic composites. Molecular assemly of these biomimetic systems based upon association of weak non-covalent bonds, including hydrogen bonds, electrostatic interactions, π-π stacking, hydrophobic forces, nonspecific van der Waals forces, and chiral dipole-dipole interactions. Although these forces are relatively weak individually, when combined, they can govern the assembly of molecular building blocks into superior and ordered structures. The main aim of our studies is to utilize molecular assembly in the design and fabrication of new functional structured materials on the micro- and nanoscale. Particularly, we are devoted to directly utilize biological units themselves to construct hybrid nanostructured materials so that some of the manufacturing difficulties of biomimetics can be avoided.

Self-Assembly of Dipeptide Nanostructures

Some peptide molecules have been found in living organism to be able to self-assemble into various structures such as vesicles, tubes, fibrils etc. Inspired by this biological phenomenon, some smart supramolecular systems could be fabricated via molecular self-assembly. Currently, our group designs a type of small cationic dipeptide as building block. We found that this type of small cationic dipeptides can self assemble into nanotubes or vesicles (**Fig. 1**). Interestingly, the transition between tube and vesicle structures could occur spontaneously under a certain condition. We investigated the conversion process quantitatively and built up a theoretical model. Such a conversion could readily bring genes into cells through the membrane. Additionally, these cationic dipeptides can also self-assemble into various types of fibrils, strands and tapes in organic solvents via weak intermolecular interactions (**Fig. 1**). and intertwist further to form gels. Such gels can be used to encapsulate quantum dots and other inorganic particles through gelating the organic solution of nanocrystals.

The self-assembly dipeptide nanostructure can be exploited as a new class of molecular transporter for the delivery of a wide range of foreign substances such as drugs, proteins and other materials. Currently, we are designing and synthesizing cationic dipeptide derivatives containing special functional units, and thus form organized nanostructures like nanowires, nanotubes or vesicles can be obtained under a certain condition. At the same time they respond to environmental stimuli such as light, temperature, electronic or magnetic ones.

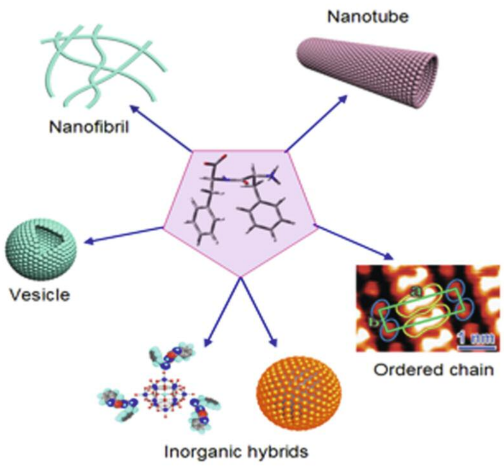

Fig. 1. Schematic representation of various nanostructures formed by self-assembly of FF-based building blocks.

Transportation of Assembled Capsules Driven by Motor Proteins

The linear molecular motor, kinesin, transports chemical payloads along microtubules in the cell. The used growing filament, a microtubule, is polar and has two functions: provide rails or tracks for the kinesin motors and limit the movement into 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 biomolecular motors, stepping motor proteins, kinesin and the complete assembly of the system. We try to provide experimental evidence how the molecular motors generate pull forces to drive 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. For instance, we recently fabricated an active biomimetic system based on the microcapsule-kinesin motor-microtubule complex. In this active biomimetic system, the microtubules act as shuttles that transport the attached polymer microcarriers. We found that the velocity of the movement does not depend on the size of the capsules but the fraction of mobile capsules depends on capsule size and biotinylation proportion of microtubule. The microtubule could also propel dextran-filled capsules to transport the internal components on the activated surface. The study integrates artificial materials into the kinesin-microtubule system and provides a potential use for straightforward and facile transport of polymer materials and fabrication of hybrid microdevices for biochemical sensing and delivery applications (**Fig. 2**).

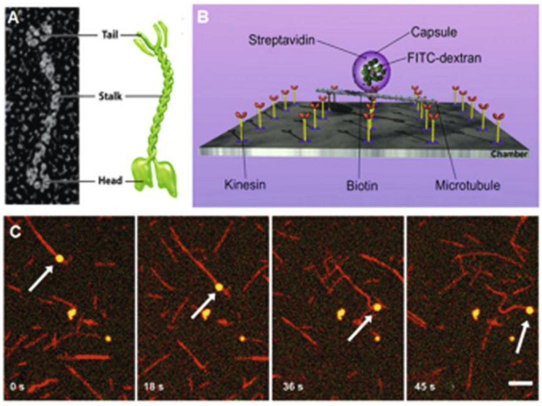

Fig. 2. layer-by-layer assembled capsule as a cargo pulled by a microtubule along the kinesin-modified channel. (A) Structure of kinesin motor protein; (B) Transport of a polymer microcapsule filled with dextran by a microtubule on a kinesin-coated surface. The capsule is coated by streptavidins, thus bound to a biotinylated microtubule. Such a microtubule carrying microcarrier can run on a kinesin-coated surface in the presence of ATP; (C)Time-lapse images of a microcapsule runs on the kinesin-coated surface. Scale bar = 5 μm. The moving microcapsule is pointed out by the white arrows.

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Supramolecular Architectures

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Although typical (hydrophilic/hydrophobic) amphiphiles such as surfactants and lipids are well matured and the formation mechanism of their nano/microscopic structures is well understood, our uncommon hydrophobic amphiphiles (π-moiety and hydrophobic alkyl tails) have more possibilities to create versatile assembled architectures and function because of their dependence on the specific organic solvent. Therefore 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 the hierarchical assembled systems should inspire further studies for supramolecular chemistry, biomimetic structures, nanotechnology as well as their materialization.

Self-assembly utilized in our group is controlling supramorphologies, which are the architecture and dimensionality of hierarchical fullerene superstructures by varying the nature of the solvent system. To achieve hierarchical fullerene-C_{60} assemblies, we have developed a series of hydrophobic-amphiphilic (solvophilic) C_{60} derivatives that bear long aliphatic chains. We explored them by using the two different intermolecular forces, π-π (C_{60}) and van der Waals (aliphatic chains) interactions. By varying the solvent system, the derivatives self-organized into various unique structures such as flakelike or flowerlike spheres, spiral and conical objects (**Fig. 1**) **[1-4]**. The finding suggests possible synthetic methodologies towards dimension-controllable nanocarbon materials.

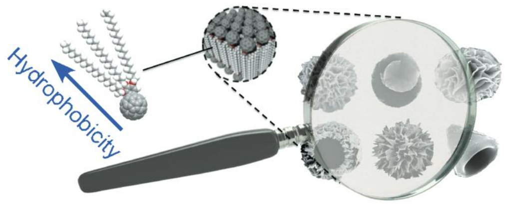

Fig. 1: Illustration of an alkylated fullerene derivative and its self-organized architectures.

A diacetylene-functionalized C_{60} derivative (1) self-organizes into flakelike microparticles. The assembled objects have more potential to be useful materials due to their quantitative yields, well-analyzed nano-assembled architectures, and their ease of hierarchical fabrication onto substrates. Both the diacetylene and C_{60} moieties can be effectively cross-linked, which leads to supramolecular materials with remarkable resistivity to solvents, heat and mechanical stress **[5]**. Moreover, the surface of the cross-linked flakelike objects is reminiscent of the Lotus Leaf as well as feature highly durable and water-repellent superhydrophobicity (**Fig. 2**). In addition, taking into account the moderate hydrophobic nature of the C_{60} surface compared to the high hydrophobicity of the hydro- or fluoro- carbons, it is suggested that the C_{60} moieties are exposed to the outer surface in the supramolecular objects formed from polar solvent conditions and defines their non-wetting properties **[6]**.

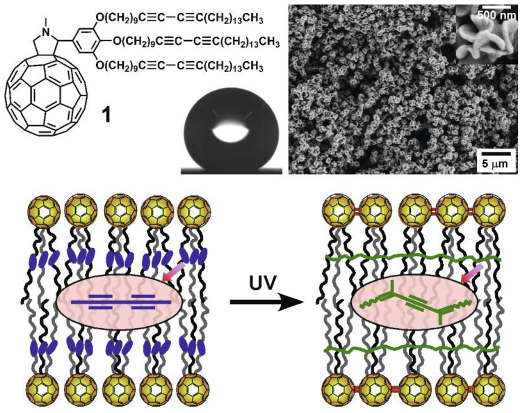

Fig. 2: A cartoon representation of the photo-cross-linking process in the bilayer structural subunit of 1. SEM image of flakelike microparticle assemblies of 1 and a photograph of a water droplet on the surface, contact angle ~ 150°.

A sustainable method for the fabrication of metallic surfaces with rose flowerlike fractal morphology was developed by using the supramolecular microparticles of **2**, possess on a nanoflake structure at the outer surface, as template (**Fig. 3**). 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 (SERS). The enhancement factor is around 10^5 **[7]**.

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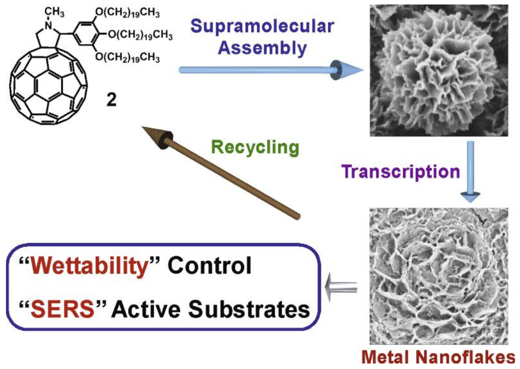

*Fig. 3: Schematic illustration of the fabrication of metal nanoflake surfaces via supramolecular assemblies of fullerene derivative (**2**) as template objects.*

Another useful application of flakelike microparticle of **2** is a "temperature indicator" for photothermal conversion of carbon nanotubes upon NIR light irradiation **[8]**. This has been constructed as an assembly of micrometer-sized, **2**-carbon nanotube hybrid, and is based upon the notion that temperature rise can be confirmed via the melt-induced morphological change of the nanocarbon assembly (**Fig. 4**). Considering that carbon nanotubes are widely used in biology for local heating, with operations conducted around body temperature, our studies serve as a reminder that NIR light irradiation of carbon nanotubes can induce an extreme temperature rise as high as 220 °C.

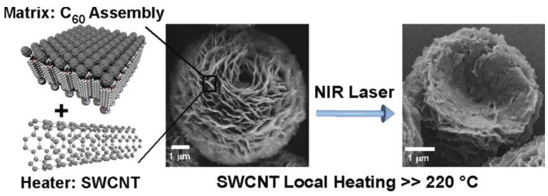

Fig. 4: Scheme of a temperature indicator for NIR photothermal conversion (>> 220 °C) of SWCNT in an assembly of 2 with flakelike microparticle structure.

In addition, our C_{60}-derivatives satisfy the requirements for high carrier mobility in the C_{60}-containing liquid crystalline (LC) materials: a high C_{60} content up to 50% and a highly ordered mesophase. Thermotropic LC of **2** shows texture under a polarized optical microscope (**Fig. 5**). It features comparably high electron carrier mobility, ~3 x 10^{-3} cm^2/Vs, making it an attractive component for C_{60}-based photoconductive soft materials **[9]**. More importantly, simple boxlike electronic density profile models are proposed to explain the relative intensity of the very rich Bragg peaks present in the XRD pattern (**Fig. 5**). The molecules arrange themselves in bilayers with their long axis on average perpendicular to the plane of the layers. Further detail structural analysis has been allowed by using this model **[10]**.

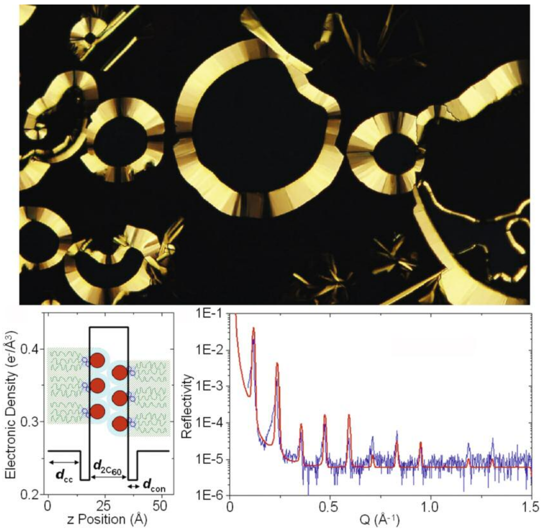

*Fig. 5: Texture of mesophase of **2** under POM. Three-box electronic density profile and comparison between corresponding model (red line) and experimental (blue line) XRD patter for **2** in the mesophase*

Another area of interests includes photoconductive crystalline fullerene materials **[11]**. Anisotropic photoconductivity of millimeter-sized flat sheet fullerene crystals obtained through arene-perfluoroarene interaction.

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