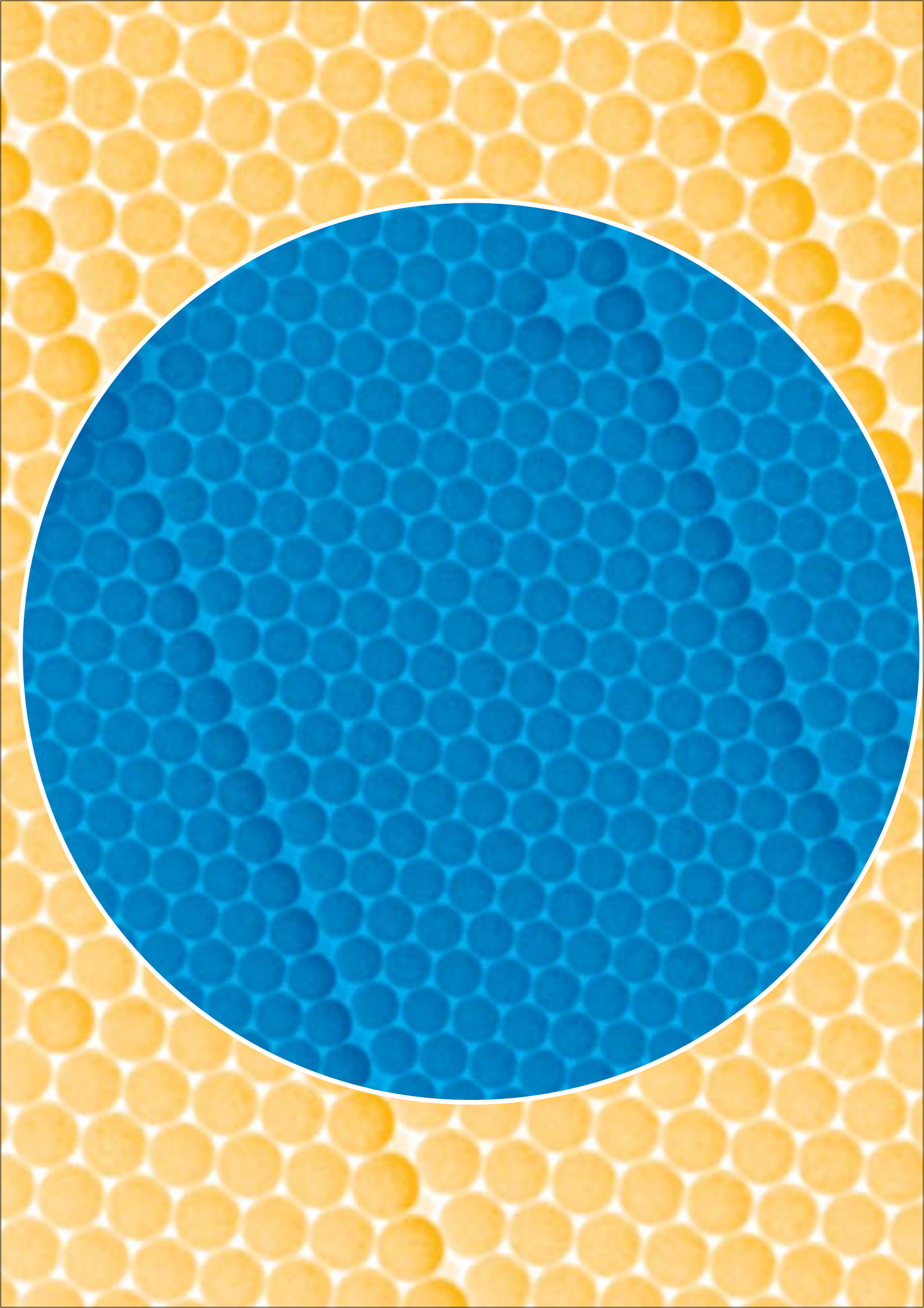
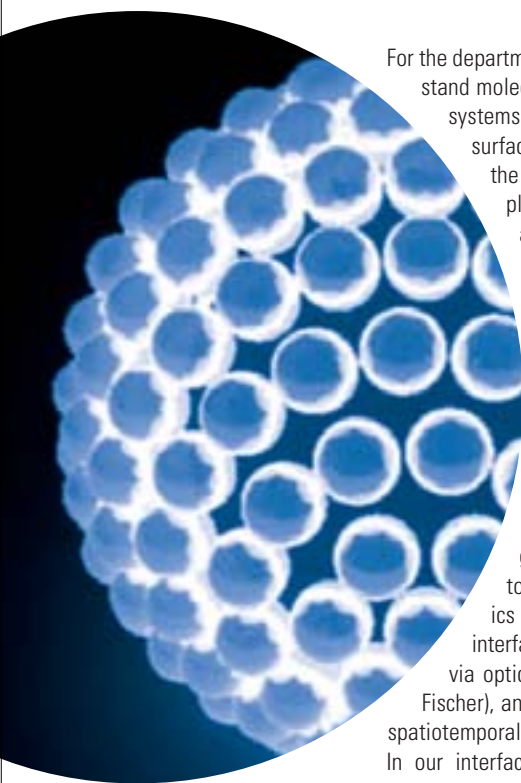


INTERFACES

INTERFACES



Research in the Department of Interfaces



For the department "Interfaces" prime motivation is to understand molecular interfaces and to relate this to colloidal systems who are by nature determined by the large surface/volume ratio. Consequently the strength of the department in characterizing planar or quasi-planar interfaces has been increased and in addition it has been tried successfully to transfer this knowledge to curved interfaces. From this we have again learned about planar interfaces since surfaces could be studied by techniques requiring large surface area (NMR, DSC).

To be more specific the methods to analyze interfaces in molecular detail could be extended by studying defects by sum frequency generation and the molecular dynamics by optical second harmonic generation (H. Motschmann). This is expected to shed light into modelling of interface dynamics (R. Miller, K.-D. Wantke). 2 D peculiarities of interface rheology and wetting have been studied via optical tweezers and fluorescence microscopy (T. Fischer), another specific interfacial phenomenon that of spatiotemporal oscillations could be modelled (D. Vollhardt). In our interfacial research there is a general trend that

amphiphiles increase in complexity, and interactions with the subphase gain importance. Consequently I tend to enhance the work of the Brezesinski group on coupling of monolayers to enzymes and to polyelectrolytes. These liquid films have remained an interesting system to study interactions between amphiphilic interfaces and their consequences for properties like gas permeation (H.-J. Müller).

In the area of coated colloids we have extended our leadership in building hollow capsules by contributing to the understanding of internal film structure (M. Schönhoff), micromechanics and adhesion (G. Sukhorukov, A. Fery). Other exciting (and related) questions concern controlled and switchable permeation and physics and chemistry in nanocontainers (G. Sukhorukov). Expanding this work should help approaching the central vision of the department, an "artificial cell". It combines almost all aspects of colloids and interfaces. One aspect of a cell is also the formation of particles inside which should be the expansion of the Riegler group now studying crystallization and growth for alkanes at model surfaces. Applying colloid chemical techniques to assemble functional molecules and clusters has already let to interesting device aspects like sensors and electrochromic displays (D. Kurth). Overall the strategy in the area of curved surfaces will be to concentrate on basic sciences and interfacial aspects but help other groups and companies develop appli-

cations. As a consequence we have acquired many large projects with application oriented partners in areas like “biotechnology” and “complex systems” where our part remains basic understanding and studying model systems. Also with this intention we have founded a joint research group with the neighbouring Fraunhofer Institute of Applied Polymer Science.

One of the strengths of the department has been to develop new methods for interface characterization. This has been in the past to introduce *surface x-ray diffraction* and *fluorescence microscopy* and now has been expanded to introduce new ways of *dynamic surface pressure* measurements and to combine this with *second harmonic generation* and *sum frequency generation*. These techniques have been added to the traditional ones:

- Brewster Angle Microscopy
- Film balance and surface potential studies
- Ellipsometry, x-ray and neutron reflectivity
- Fluorescence and absorption spectrometry
- Scanning Force and colloidal probe microscopy
- Fluorescence recovery after photobleaching (FRAP)
- Fluorescence correlation spectroscopy
- FTIR-spectroscopy
- Confocal fluorescence and Raman microscopy
- Single particle light scattering

- Zeta potential studies
- Zyklovoltammetry
- Quartz crystal microbalance measurements
- NMR measurements, in special solvent relaxation
- Oscillating bubble and pendent drop tensiometry
- Thin film balance studies

We regret having lost the staff members H. Hermel and D. Vollhardt because of retirement and are glad that E. Donath (Leipzig), M. Gao (Beijing) and F. Caruso (Melbourne) received professor positions. I hope for more of this good news the following years. Because the shrinking of the department had to start with the expectation of our forth department only E. Donath has been replaced as a group leader (by G. Sukhorukov).

Major awards have been the Sofia-Kovaleskaja Award to G. Sukhorukov and the Federation Award to F. Caruso. I have been honoured by the British Colloid group with the “Founder’s Lecture” and by the Japanese Chemical Society with the “Lectureship Award”.

[Prof. Helmuth Möhwald](#)
[Director of the Department of Interfaces](#)

Interactions in Complex Monolayers



Generic Phase Diagrams of Special Phospholipids

[In cooperation with F. Bringezu (Leipzig), B. Dobner (Halle)]

Aim: The aim of this work was a generalized description of the monolayer behavior of systematically modified lipids.

Results: Condensed phases of chemically modified triple-chain phospholipids were characterized by grazing incidence x-ray diffraction (GIXD). Increasing chain length corresponds to a temperature effect, which was quantified for different lipids depending on the head group structure using pressure/area isotherm (2D systems) and DSC (3D systems) measurements. The combination with structure investigations revealed generic phase diagrams (Fig. 1).

We found the first experimental evidence of the unusual τ phase in multiple-chain lipid monolayers, which exhibits an undistorted in-plane lattice despite of tilted chains.

Stepwise Collapse of New Silicon Polymer Films

[In cooperation with Yu. K. Godovsky (Moscow), T.R. Jensen (Risoe), K. Kjaer (Risoe)]

Aim: This project presents the first "in-situ" structural investigation of the stepwise collapse of cyclolinear polyorganosiloxane (CL-POSi) monolayers during compression.

Results: In the uncompressed state, BAM images demonstrate partial surface coverage by solid-like birefringent monolayer islands, which is consistent with a simple model of aligned extended polymer chains lying on the water surface in a quasi-two-dimensional "nematic-like" liquid crystalline arrangement. The plateaus in the isotherm observed on continuous compression indicate the gradual formation of multilayers. One diffraction peak has been observed at zero surface pressure (Fig. 2, top) as well as at higher pressures (Fig. 2, bottom). The repeat distance corresponds to the inter-chain axes distance. The lateral positional correlation between parallel chains ranges from about 6-7 for the monolayer to about 25 interchain distances for the multilayers. The thickness of the layers determined from the Bragg rods is consistent with X-ray reflectivity measurements (Annual Report 2000).

Ordering of Model Compounds of Phosphoinositides in 2D- and 3D-Systems

[In cooperation with R. Klinger (Jena)]

Aim: Phosphoinositides (PIs) appear to be involved in the signaling pathways that trigger a wide range of cellular processes. Our aim is to analyze the phase and mixing behavior as well as the phosphorylation reactions of PIs.

Results: Structural studies require chemically well-defined PIs. Since synthetic PIs are difficult to obtain, model compounds having similar interfacial properties have been

investigated. The first step in this long-term study is the investigation of lipid ordering in 2D- and 3D-systems. 1, 2-Distearoyl-phosphatidylcholine (DSPC) was mixed with an unsaturated lipid [either 1-stearoyl-2-arachidonoyl-glycerol (SAG) or 1-stearoyl-2-arachidonoyl-phosphatidic acid (ASPA)]. In contrast to ASPA, SAG molecules are miscible with DSPC in mono- and bilayers and modify strongly the ordering of DSPC chains. Increasing SAG concentration leads to a more and more upright orientation of the acyl chains (Fig. 3). Our experiments show that the presence of a second layer modifies the ordering in both layers.

Interactions of Amyloid β with Interfaces

[In cooperation with A. Thünemann (Golm)]

Aim: Amyloid β ($A\beta$) is an amphiphilic peptide that exists mainly in α -helical conformation. In β -sheet conformation, the peptide can aggregate and form the amyloid fibrils found in cerebrovascular deposits and neuritic plaques observed in Alzheimer's disease. Since $A\beta$ is amphiphilic, interactions with phospholipids or other interfaces could play an important role for $A\beta$ folding and toxicity.

Results: $A\beta$ conformation in solution is highly dependent on the solvent, pH, ionic strength and a number of other parameters. The simplest way to achieve a non-aggregated conformational state is dissolution in a solvent, which disrupts intermolecular H-bonds such as halogenated alcohols. After evaporation of the solvent and dissolution in water, $A\beta$ adopts a mainly random coil conformation. At 37 °C, the peptide conformation is converted with time into β -sheet. It is known that negatively charged micelles formed by SDS and fluorinated alcohols such as trifluoroethanol are capable of converting the β -sheet structure of the peptide into α -helix. Therefore, negatively charged fluorinated nanoparticles were prepared and their interaction with $A\beta$ peptide is being characterized. Also the type of the surface (hydrophilic or hydrophobic) has a large influence on the α - β transition.

Adsorption of $A\beta$ to a DPPC monolayer as a model membrane and to the pure air/water interface was measured using the Wilhelmy method. An equilibrium surface pressure of ~16 mN/m was reached in both cases (Fig. 4). The plateau at 5 mN/m represents the LE/LC transition of DPPC induced by the penetration of $A\beta$. The formation of condensed phase domains was registered by BAM.

Further compression resulted in a second smooth plateau at approximately 30 mN/m and finally the molecular area of pure DPPC was reached indicating the squeezing-out of $A\beta$ from the monolayer. The secondary structure of $A\beta$ was investigated by Fourier Transform Infrared Spectroscopy (FTIR). The amide I and amide II bands, which were found after adsorption to both pure water surface and to a DPPC monolayer, are characteristic for β -sheet conformation (Fig. 5). Hence the transition from mainly random coil to mostly β -sheet occurs during the adsorption process.

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1974: Diploma, Biophysics

(Lomonossov University of Moscow)

Thesis: The parametric pump – a physical-chemical model of the active transport of ions in cells

1981: PhD, Physical Chemistry

(Martin Luther University of Halle/S.)

Thesis: Einfluss der chemischen Struktur auf das thermische Phasen- und Mischungsverhalten binärer und ternärer Phospholipid-Wasser-Systeme

1987: Habilitation, Colloid Chemistry

(Martin Luther University of Halle/S.)

Thesis: Untersuchungen zum Phasen- und Mischungsverhalten ausgewählter Phospholipid-Wasser-Systeme

1981-1982: Postdoc (Biological

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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, Golm)

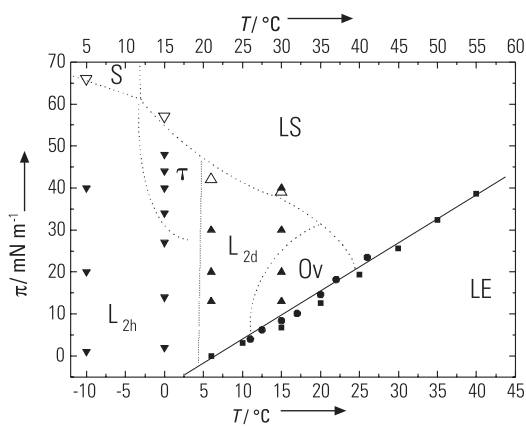


Fig. 1: Generic phase diagram of 1-O-hexadecyl-2-acyl-glycero-3-phosphocholines

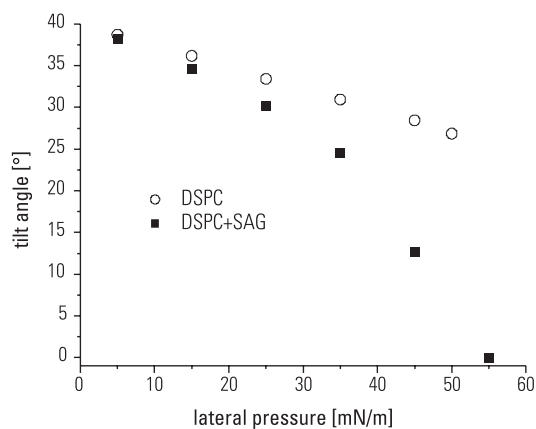


Fig. 3: Tilt angle as a function of film pressure at 20 °C for DSPC and for DSPC mixed with SAG, mimicking PI

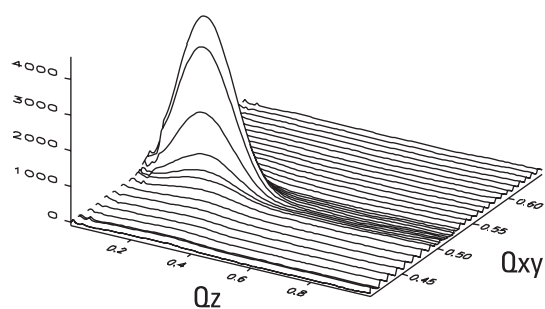
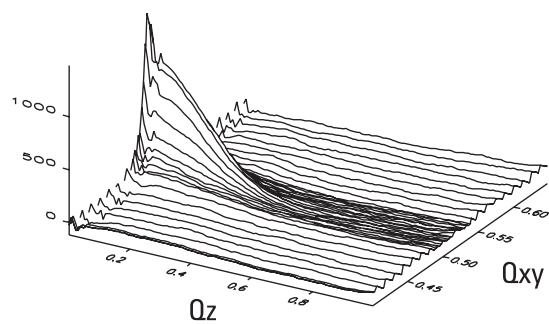


Fig. 2: Diffracted intensity as function of in-plane and out-of-plane scattering vector components Q_{xy} and Q_z at 0mN/m (top) and 10mN/m (bottom) for a cyclolinear polysiloxane monolayer

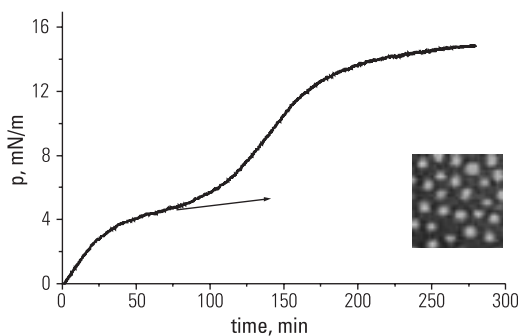


Fig. 4: Adsorption kinetics of $A\beta$ and BAM image (right)

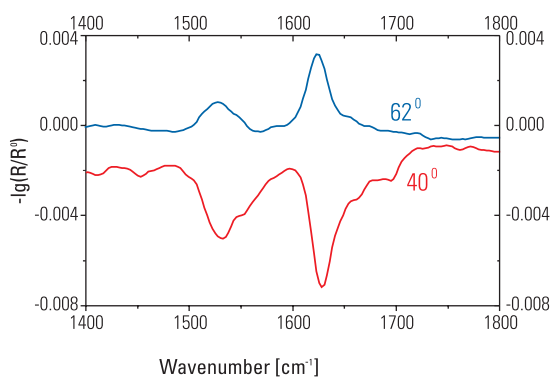


Fig. 5: FT-IR spectra at the air/water interface for $A\beta$ monolayers using p-polarized light at different angles of incidence

Key Publications:

- [1] Estrela-Lopis, I., Brezesinski, G. and Möhwald, H.: DPPC/Phospholipase D interactions investigated with PM-IRRAS. *Biophys. J.* 80, 749–754 (2001).
- [2] Brezesinski, G., Müller, H.J., Toca-Herrera, J.L. and Krustev, R.: X-ray diffraction and foam film investigations of PC-headgroup interaction in water/ethanol mixtures. *Chem. Phys. Lipids* 110, 183-194 (2001).
- [3] Bringezu, F., Dobner, B. and Brezesinski, G.: Generic phase behavior of branched-chain PL monolayers. *Chem. Eur. J.* 8, 3203-3210 (2002).

Analysis – Synthesis – Purification of Amphiphiles



Effect of Counter Ions on the Behavior of Soluble Anionic Surfactants

Aims:

- Effect of different counter ions in alkyl sulfates on the adsorption at the water/air interface
- Calorimetric investigation of the counter ion effect on the micellization process of alkali alkyl sulfates

Results:

The equilibrium surface tension of decylsulfate with various monovalent (alkali) counter ions was investigated. It was found that the surface activity of surface chemically pure decylsulfate significantly increases with decreasing hydrated size of the counter ion. **Fig. 1** presents the dependence of the surface tension of decylsulfate on its counter ion in solution for five monovalent cations. The surface tension is most effectively decreased in presence of the Cs⁺-counter ion.

Thermodynamics of micelle formation of anionic surfactants was investigated by using isothermal titration calorimetry (ITC). Highly purified decyl and dodecyl sulfates have been used to analyze the effect of counter ions (Li⁺, Na⁺, K⁺, Cs⁺). Critical micelle concentration (cmc) and enthalpy of demicellization were systematically determined between 10 °C and 60 °C. The decrease of the cmc in the order Li⁺>Na⁺>K⁺>Cs⁺ for a fixed chain length (**Fig. 2**) is related to the decrease of the degree of ionization of the –SO₄⁻ M⁺ bond. The electrostatic repulsions between ionic head groups prevent the aggregation but are progressively screened as the ionic character decreases with the size of the counter ion. Temperature changes cause large variations of ΔH_{mic} and ΔS_{mic} , whereas ΔG_{mic} remains almost constant. The enthalpy of micellization decreases strongly with increasing temperature (**Fig. 3**) passing through zero (endothermic to exothermic). At a given temperature, ΔH_{mic} decreases with the size of the counter ion. This finding is directly related to the energy required to overcome the electrostatic repulsion between head groups.

Behavior of Nonionic Surfactants in the Water/Hexane System at Different Temperatures

Aims:

The adsorption kinetics of surfactant molecules at the water/hexane interface is accompanied by a transition of molecules across the interface. The transition rate depends on the distribution coefficient (Kp) of the surfactant in the system hexane/water. The distribution coefficient for the alkyl polyoxyethylene surfactants C_nEO_m is expected to depend on the length of the alkyl chain C_n and on the number m of EO groups. Kp can be directly determined by quantitative high performance liquid chromatography (HPLC).

Question: How do the distribution coefficients determined analytically for different temperatures and concentrations depend on the molecular structure of the surfactant?

Results:

The results concerning the distribution of nonionic surfactants in the water/hexane system are consistent with the partial lipophilic character of the polyoxyethylene chain and with the strong influence of the carbon chain on the surfactants properties. Kp decreases strongly with the temperature. In the concentration range below the cmc the distribution coefficient is independent of concentration. With increasing number of EO groups the temperature dependence of Kp becomes steeper. A ring structure in the molecule corresponds to effectively four CH₂ groups in an aliphatic chain (**Fig. 4**).

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1964: Diploma, Chemistry

(Humboldt-Universität Berlin)

Thesis: Synthesis and sulfation

of Ricinolic- and 12-Hydroxystearic acid-n-alkyl esters of the chain length C1-C6

1968: PhD, Chemistry

(Humboldt-Universität Berlin)

Thesis: Synthesis of anionic surfactants

by sulfation of N-substituted

amides of 12-Hydroxyoctadecanoic acid,

12-Hydroxyoctadecenoic-(9)-acid and

11-Hydroxyundecanoic acid

1981-1982: Study of Colloid Science

(Technische Universität Dresden)

1964-1991: Central Institute of Organic

Chemistry of the Academy of Sciences

Since 1992 : Group Leader

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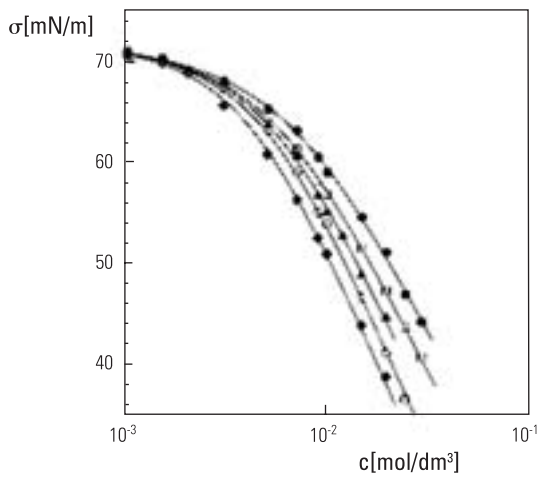


Fig. 1: The dependence of the surface tension of LiDS – black circles, NaDS – white squares, NH₄DS – black triangles, KDS – white circles and CsDS – black diamonds, on their concentration. Lines represent fits of the theoretical model of adsorption of ionic surfactants to experimental data.

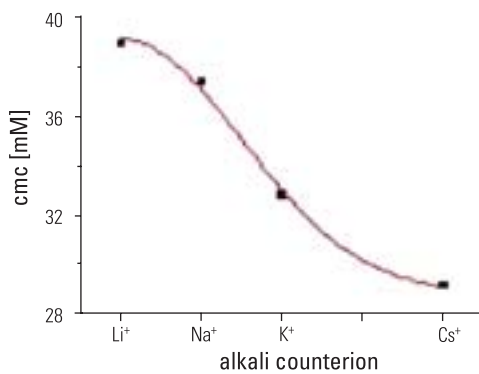


Fig. 2: cmc of decylsulfates versus alkali counter ion

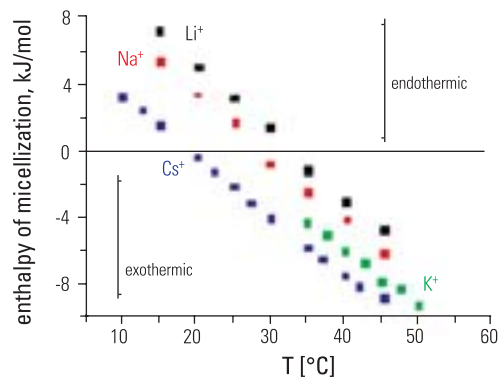


Fig. 3: ΔH_{mic} of decylsulfates with different alkali counter ions versus temperature

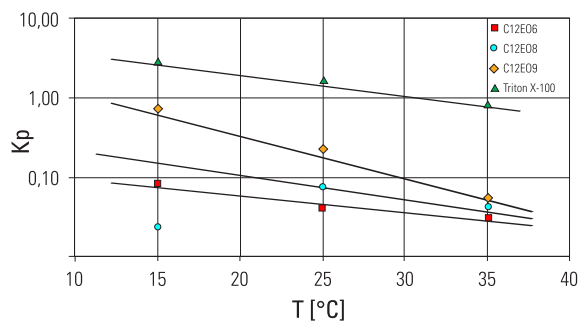
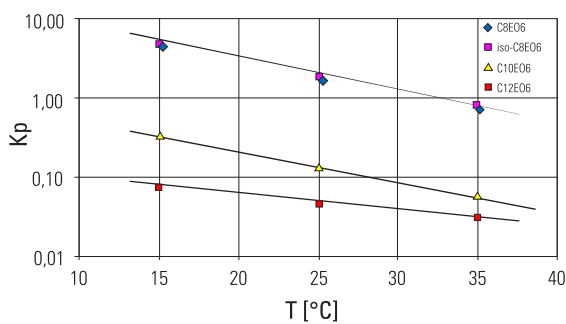


Fig. 4: Partition coefficients at the hexane / water interface of selected C_nEO_m as a function of temperature of T; $K_p(T) = \frac{C_W}{C_H}$

Key Publications:

- [1] Czichocki, G., Dautzenberg, H., Capan, E. and Vorlop, K.-D.: New and effective entrapment of polyelectrolyte-enzyme-complexes in LentiKats, *Biotechnology Letters* 23, 1303-1307, (2001).
- [2] Miller, R., Fainerman, V. B., Makievski, A. V. and Czichocki, G.: Temperature Dependence of the Equilibrium and Dynamic Surface Tension of Oxyethylated p-tert. Butyl Phenol Solutions, *Tenside Surf. Det.* 38, 173-178, (2001).
- [3] Warszynski, P., Lunkenheimer, K. and Czichocki, G.: Effect of counter ions on the adsorption of ionic surfactants at fluid-fluid interfaces, *Langmuir* 18, 2506-2514, (2002).
- [4] Ropers, M. H., Czichocki, G. and Brezesinski, G.: Counter ion effect on the thermodynamics of micellization of alkyl sulfates, *J. Phys. Chem.* (in press).

(QUASI) PLANAR INTERFACES - FLUID INTERFACES

Static and Dynamic Peculiarities of Two Dimensional Systems (Langmuir Monolayers)



Aims:

Langmuir monolayers exhibit hexatic phases, which are characteristic for 2D-systems. Due to long range hydrodynamic interactions of 2D-systems transport properties of Langmuir monolayers are intimately coupled to the 3D subphase. It is the aim of our research to understand such kinds of peculiarities of the phase behavior and of rheological properties of Langmuir monolayers.

Results:

Modulation Crack Growth and Crack Coalescence upon Langmuir Monolayer Collapse

An extensive study for Langmuir monolayers' collapse is carried out to explore the generality of classification of their crack patterns and to analyze crack kinetics in the anisotropic cracks. Upon compression of fatty acid monolayers beyond the collapse pressure three classes of fracture patterns, a surface roughening, random crack network or anisotropic fracture can be observed depending on chain length of the fatty acid, pH value and ion concentration of the subphase. A statistical characterization of the anisotropic crack growth of Langmuir monolayer fracture is presented. Anisotropic cracks grow on a Co^{2+} water subphase as quasi-periodic modulations, branching off previously formed cracks, interrupted by the coalescence of modulation cracks. Slight changes in pH and concentration of Co^{2+} ions in the subphase cause drastic changes of the modulation crack coalescence rate. We suggest that differences in the viscoelastic nature of the monolayer are the main causes for the three types of crack growth scenarios.

Shapes of Langmuir Monolayer Domains in Confined Geometries

The shape of two dimensional liquid expanded droplets of a methyl octadecanoate Langmuir monolayer confined in gas cavities in a liquid condensed matrix is studied using fluorescence microscopy. Confinement destabilizes the circular shape by increasing the dipole density of the liquid expanded phase or by decreasing the bare line tension λ between the liquid expanded and the gaseous phase. Confinement causes a cascade of shape transitions from a circular droplet towards shapes of n-fold symmetry with increasing n until the droplet returns to a circle as its size approaches the size of the cavity. The experiments are explained theoretically and it is shown that the three phase coexistence region is not an equilibrium phase coexistence region. Material parameters depend on the relative area fraction of the coexisting phases.

Wetting in Asymmetric Quasi-2 Dimensional-Systems

The effect of electrostatic dipole interactions on the wetting behavior of two dimensional droplets, approximated by circular segment shapes with contact angle α is investigated. α depends on the geometric structure far away from the three-phase contact point. We theoretically find metastable α values associated with transitions from complete wetting to partial dewetting, triggered by minute changes of the film area, the surface potential of the coexisting phases, or their line tensions. The predictions are confirmed experimentally in a Langmuir monolayer model system. The wetting instability may influence intramembrane biochemical reactions between protein species dissolved in coexisting phases via the length of the contact line between the phases, the only region where chemical reactions between the species are possible.

Cavitation of Langmuir Monolayers

Cavitation in liquid expanded and liquid condensed Langmuir monolayers induced by laser heating or microbubble coalescence is studied experimentally using fluorescence and Brewster angle microscopy. The kinetics of hole closure of 2D gaseous cavitation bubbles exhibits a decelerated dynamics for cavities surrounded by liquid expanded phase and an accelerated dynamics for cavities in liquid condensed phase. Most of the cavities in liquid condensed phases possess a nonconvex shape and do not close. The results are compared with theoretical predictions derived for 2D-cavitation of liquid monolayers of different surface shear viscosities, and solid monolayers with diffusive flux of vacancies and interstitials. While part of the theory is in qualitative agreement with the experiment the experimentally observed hole persistence within the liquid condensed phases and the hole closure within liquid expanded phases remains to be explained. The technique of microbubble coalescence might be particularly useful for the study of the rheological properties of hexatic phases.

Electrophoretic Relaxation Dynamics of Domains in Langmuir-Monolayers

Equilibrium patterns of a Langmuir monolayer of methyl octadecanoate are perturbed on a micrometer length scale using optical tweezers and laser heating. The consecutive electrophoretic motion of circular domains in liquid expanded or gaseous surroundings is investigated. The experimentally observed domain relaxation is described by a balance of the dissipative hydrodynamic force on the domain and an electrostatic dipole force from a neighbored domain. Drag forces derived from the experiments are in agreement with theoretical predictions for the viscous drag on solid domains moving in monolayer surroundings of negligible surface shear viscosity.

The dipole interactions are characterized by the surface potential differences between the coexisting phases. On pure water the relaxation experiments reveal that the surface potential difference between the liquid condensed and the liquid expanded phase depends on the area fractions and the coexistence cannot be described by an ideal first order phase transition with constant dipole densities of the phases.

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1989: Diploma, Theoretische Physik
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Thesis: Einfluss der Dipolwechselwirkung auf dynamische Messgrößen in Ferro- und Antiferromagneten

1992: PhD, Physics (Max-Planck-Institut für Polymerforschung, Mainz)

Thesis: Wärmeleitfähigkeit dünner Polymerfilme und Wechselwirkung periodisch strukturierter Grenzflächen mit Oberflächenpolaritonen

1992: Postdoc, Supramolekulare Physik (Johannes Gutenberg University, Mainz)

1993-1994: Feodor Lynen Stipendiat (University of California Los Angeles)

1999: Habilitation, Experimental Physics (University of Leipzig)

Thesis: Der Langmuir-Monolayer, ein quasi zweidimensionales System im thermodynamischen Gleichgewicht und Nichtgleichgewicht

Since 1999: Group Leader, Heisenberg Fellowship (Max Planck Institute of Colloids and Interfaces, Golm)

Equilibrium Size of Circular Domains in Langmuir-Monolayers

Calculations of equilibrium radii of Langmuir-monolayer domains are compared with measurements in the liquid expanded/gas coexistence region of myristic acid. This paper extends the works of McConnell to higher area fractions Φ of the domain phase. A maximum increase of the equilibrium radius of gas-domains by a factor of 26 on expansion is predicted, while the number-density of the domains passes through a maximum at $\Phi=0.35$. The experiments agree with these predictions. Some domains disappear on expansion before domains actually touch each other. A quantitative analysis shows that the line tension between both phases increases by about 10% on expansion.

Liquid Crystalline and Solid Stripe Textures in Langmuir Monolayers

Textures of the molecular orientation of molecules in a Langmuir monolayer of pentadecanoic acid (PDA) are compared with similar textures of monomeric and polymeric pentacosadiynoic acid (PCA) monolayers. Both acids PDA and PCA (monomeric and polymeric) exhibit stripe textures with characteristic modulations of the molecular orientation. Using laser heating we may cleave or deform the stripes in monomeric PCA. The relaxation of the stripes reveals that the stripes in monomeric PCA are solid stripes with a finite Young's modulus of the order $E=5-30\text{mN/m}$ in contrast to those in PDA, which are hexatic with a vanishing Young's modulus.

Stability Criteria for 2 Dimensional Wetting in Monolayers

2D-Pendant liquid expanded droplets partially wet liquid condensed/gas phase boundaries in methyl octadecanoate Langmuir monolayers. Their shape is described by the Young-Laplace equation including long-range electrostatic interactions on a scale Δ . It is invariant under shape invariant scale transformations. We show that the local stability at the three phase intersection point is described by Young's equation for the contact angle. The contact angle is not invariant under shape invariant scale transformations but is a material's constant at a fixed scale-parameter Δ . By comparison of numerically simulated droplets with experimental droplets observed with a fluorescence microscope we determine the spreading coefficient of wetting Langmuir monolayer phases as well as a lower limit for Δ . We find $0.12\ \mu\text{m} < \Delta$, and suggest that the scale parameter shall be interpreted as dipolar correlation length, not as a molecular cut-off length.

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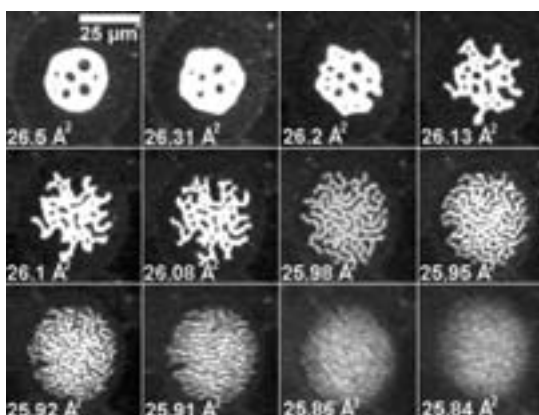


Fig. 1: Shape instability of a liquid 2D droplet. The circular droplet shape changes toward a labyrinth pattern upon confinement of the droplet.

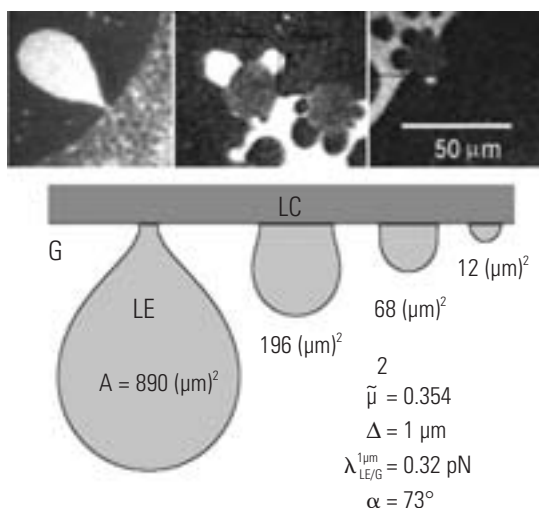


Fig. 2: Shape of electrostatically deformed pendant droplets, experiment versus theory

Key Publications:

- [1] Hatta, E. and Fischer, Th. M.: Modulation crack growth and crack coalescence upon Langmuir monolayer collapse. *J. Chem Phys. B* 106, 589-592 (2002).
- [2] Khattari, Z. and Fischer, Th. M.: Shape of Langmuir monolayer domains in confined geometries. *J. Phys. Chem. B* 106, 1677-1683 (2002).
- [3] Khattari, Z., Heinig, P., Wurlitzer, S., Steffen, P., Lösche, M. and Fischer, Th. M.: Wetting in asymmetric quasi-2d-systems. *Langmuir* 18, 2273-2279 (2002).
- [4] Khattari, Z., Steffen, P., Fischer, Th. M. and Bruinsma, R.: Cavitation of Langmuir monolayers. *Phys. Rev. E* 65 041603-1/11 (2002).
- [5] Wurlitzer, S., Schmiedel, H. and Fischer, Th. M.: Electrophoretic relaxation dynamics of domains in Langmuir monolayers. *Langmuir* 18, 4393-4400 (2002).
- [6] Wurlitzer, S., Fischer, Th. M. and Schmiedel, H.: Equilibrium size of circular domains in Langmuir monolayers. *J. Chem. Phys.* 116, 10877-10881 (2002).
- [7] Hatta, E. and Fischer, Th. M.: Liquid crystalline and solid stripe textures in Langmuir monolayers. *Langmuir* 18, 6201-6206 (2002).
- [8] Heinig, P., Wurlitzer, S., John, T. and Fischer, Th. M.: Stability criteria for two dimensional wetting in monolayers. *J. Phys. Chem. B* 106, 11951-11960 (2002).

(QUASI) PLANAR INTERFACES - FLUID INTERFACES

Thermodynamics, Kinetics and Dilational Rheology of Interfacial Layers



Aims:

The non-equilibrium properties of interfacial layers are most relevant for many technical applications, such as the understanding of disperse systems like foams and emulsions. The baseline for any dynamic or rheological study is the interfacial thermodynamics, i.e. the equation of state.

One of the targets of the present work was a systematization of experimental results for equilibrium surface tensions for non-ionic and ionic surfactants in order to discover structure-behavior relationships. For this classical as well as recently developed models for surfactant adsorption layers were used. In addition, general thermodynamic expressions were derived which allow calculation of the interfacial tension isotherm of surfactant mixtures from the adsorption data of the individual components. The derived equations account for the non-ideality of the surface layer constituents, surfactant ionization, and differences in the molar areas of the components.

Results:

The work performed allows drawing general conclusions concerning the thermodynamics and the rheological state of interfacial layers formed by adsorbed soluble surfactants.

Systematisation of Equations of State

Much attention was paid to the selection of reliable experimental data, based on the principles of high purity of the surfactants and solutions used, and control of experimental conditions under which the equilibrium was established. For the analysis four models were used: Langmuir and Frumkin isotherms, reorientation model, and surface aggregation model. To process the experimental data problem-oriented software was developed in form of a fitting program.

The characteristic parameters of adsorption layers determined for a large number of homologous series of surfactants, such as alcohols, diols, fatty acids, soaps, alkyl dimethyl phosphine oxides, oxethylated alcohols, alkyl sulphates, alkyl ammonium salts, were summarized in [1].

An equation for the adsorption equilibrium constant b is based on the increments for the polar group and the number of methylene units n_c in the hydrophobic chain:

$$b = \frac{1}{\rho\alpha^2} \exp\left(-\frac{(\Delta G_{\text{CH}_2}^0 \cdot n_c + \Delta G_{\text{P}}^0) \alpha}{RT}\right), \text{ where } \alpha = 1$$

$\Delta G^0 = \Delta G_{\text{CH}_2}^0 \cdot n_c + \Delta G_{\text{P}}^0$. The increment values of standard free energy per methylene unit $\Delta G_{\text{CH}_2}^0$ for various ionic and non-ionic surfactants vary between -2.6 kJ/mol and -3.3 kJ/mol. The free energy increment for non-oxethylated polar head groups $\Delta G_{\text{P}}^0 = -4.25$ kJ/mol does not significantly depend on surfactant nature. **Fig. 1** summarizes the experimental data of the adsorption constant b on n_c for a large number of surfactants for non-ionic and $\alpha = 1/2$ for ionic surfactants, and $\rho \approx 55.6$ [mol H₂O/l]. For the non-ionic and amphoteric surfactants the lines 1 and 2 correspond to $\Delta G_{\text{CH}_2}^0 = -(2.6 \div 3.0)$ kJ/mol, and for ionic surfactants the lines 3 and 4 correspond to $\Delta G_{\text{CH}_2}^0 = -(2.6 \div 3.0)$ kJ/mol, i.e. they agree with the generally accepted increments for non-ionic surfactants. For oxethylated non-ionic surfactants (C_nEO₈, line 5) and ionic surfactants (C_nEO₂SO₃Na, line 6) we have $\Delta G_{\text{CH}_2}^0 = -2.86$ kJ/mol and -3.3 kJ/mol, respectively.

Surface Thermodynamics of Surfactant Mixtures

The thermodynamic model derived for the description of the adsorption behavior of mixed surfactant systems requires knowledge about the surface tensions of the single compounds or their individual adsorption isotherms. The isotherm of the mixture can then be constructed without assuming any extra interaction parameter between the different compounds. The generalized Szyszkowski equation serves as the starting point

$$\Pi = \frac{RT}{\omega} \ln \left(1 + \frac{\theta_1 + \theta_2}{1 - \theta_1 - \theta_2} \right) = \frac{RT}{\omega} \ln(b_1 c_1 + b_2 c_2 + 1)$$

which can be rewritten into a simple form (1)

$$\exp \bar{\Pi} = \exp \bar{\Pi}_1 + \exp \bar{\Pi}_2 - 1.$$

Here the b_i are constants, c_i are surfactant bulk concentrations, $\theta_i = \Gamma_i \omega$ are the monolayer coverage, ω is the mean surface area, Γ_i are the adsorptions, $\Pi = \gamma_0 - \gamma$ is the surface pressure, γ_0 and γ are the surface tensions of solvent and solution, respectively.

$$\bar{\Pi} = \Pi \omega / RT, \bar{\Pi}_1 = \Pi_1 \omega / RT \text{ and } \bar{\Pi}_2 = \Pi_2 \omega / RT$$

are dimensionless surface pressures of the mixture and individual solutions of components 1 and 2, respectively, taken at the same surfactant concentrations as in the mixture. For mixtures of ionic surfactants a similar equation results.

$$\exp \bar{\Pi} = \left((\exp \bar{\Pi}_1 - 1)^2 + (\exp \bar{\Pi}_2 - 1)^2 \right)^{1/2} + 1$$

An example is shown in **Fig. 2** [2].

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1973: Diploma, Mathematics, (University of Rostock)

Thesis: Fredholm Operators

1977: Research Stay

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1978: PhD, Physical Chemistry

(Academy of Sciences, Berlin)

Thesis: Adsorption kinetics and exchange of matter of surfactants at liquid interfaces

1988: Habilitation, Physical Chemistry

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Thesis: Modelling of surfactants, surfactant mixtures and macromolecules at liquid interfaces

1990/91: NCERC Fellow

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Since 1992: Group Leader

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2002: Research Stay

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The agreement between the values calculated from the equation given above and those measured experimentally is very good.

Dilational Elasticity of Adsorption Layers

The dilational elasticity is a function of surface coverage and frequency of perturbation. All models existing so far allow understanding measured elasticities only up to a surface coverage of about 50%. At closer packing the measured values are much lower than those expected from theories. On the basis of a Frumkin isotherm and the assumption of a certain compressibility of adsorbed molecules a new model was developed. This model assumes that the molar area of a surfactant in a packed surface layer is given by the linear relationship. $\omega = \omega_0 (1 - \varepsilon \Gamma)$. The consideration of a compressibility coefficient ε yields good agreement between experimental and theoretical surface dilational elasticities (Fig. 3). The ε -values obtained from the experimental data via the developed new theory are in very good agreement with data obtained for similar but insoluble molecules via X-ray reflection studies. Note, ε only slightly affects the shape of the equation of state.

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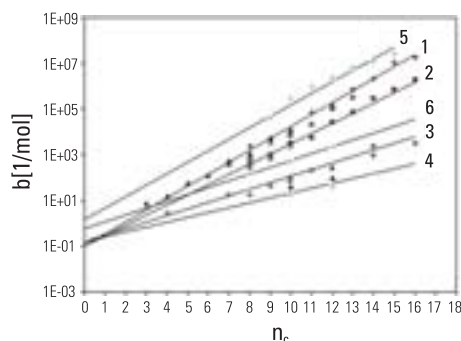


Fig. 1: Adsorption equilibrium constant b as a function of n_c for various surfactants: (\blacktriangle) C_nOH ; (\diamond) $C_n(OH)_2$; (\triangle) C_nO_2H ; (\blacklozenge) C_nDMPO ; (\blacksquare) C_nBHB ; (\square) C_nPIP ; (\times) C_nEO_8 ; ($*$) C_nO_2Na ; (\circ) C_nSO_4Na ; ($+$) $C_nEO_2SO_4Na$; (\bullet) C_nTAB ; (\blacktriangle) C_nACI ; theoretical lines are calculated with $\Delta G_{\Gamma}^0 = -4.25 kJ/mol$ [1].

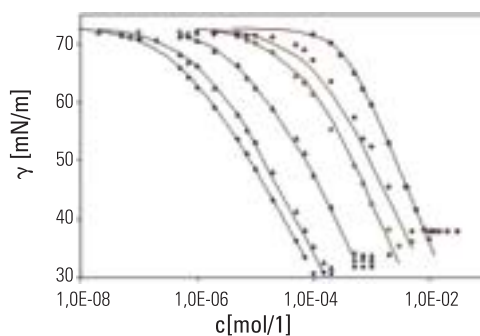


Fig. 2: Surface tension isotherms for $C_{10}EO_5$ (\diamond), SDS in 0.01M NaCl (\square) and their mixtures in 0.01M NaCl with ratios 1:1 (\triangle), 1:10 (\blacktriangle), 1:100 (\circ) and 1:500 (\bullet), solid lines are theoretical isotherms

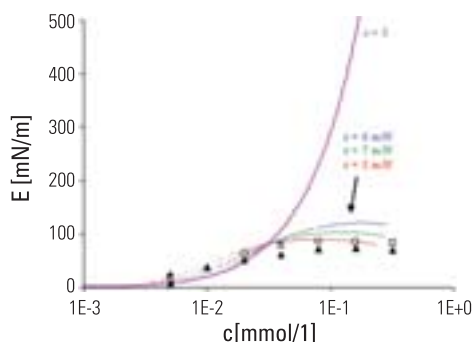


Fig. 3: Comparison of experimental surface dilational elasticity of $C_{12}DMPO$ solutions at $f > 400$ Hz (symbols, data from literature); Theoretical dependencies were calculated for different values of ε , the thick solid line refers to $\varepsilon = 0$

Key Publications:

[1] Fainerman, V. B., Miller, R. and Möhwald, H.: General Relationships of the Adsorption Behaviour of Surfactants at the Water/Air Interface. *J. Phys. Chem.*, 106, 809-819 (2002).

[2] Fainerman, V. B. and Miller, R.: Simple method to estimate surface tension of mixed surfactant solutions. *J. Phys. Chem. B*, 105, 11432-11438 (2001).

[3] Fainerman, V. B., Miller, R. and Kovalchuk, V. I.: Influence of compressibility of adsorbed layers on the surface dilational elasticity. *Langmuir*, 18, 7748-7752 (2002).

Molecular Organization in Soluble Monolayers and Functional Films



Aims:

A major focus in the work of the group is to understand the structure and the selforganization of molecules at interfaces and the impact of interfaces on bulk properties of adjacent phases. This knowledge is utilized for the design of novel structures with specific function.

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1988: Diploma, Chemistry

(University of Erlangen)

Thesis: Numerical and analytical studies on the quantum dynamical equation of Davidov Solitons

1991: PhD, Chemistry

(Max Planck Institute of

Polymer Research, Mainz)

Thesis: Scaling and adsorption

studies of Block-copolymers

1991-1993: Postdoc

(Eastman Kodak, Rochester, New York)

Since 1994: Group Leader

(Max Planck Institute of Colloids

and Interfaces, Golm)

Results:

Wetting

The formation and the shape of wetting patterns on structured surfaces have received significant attention. In these experiments a surface consisting of patches of different degree of hydrophobicity-hydrophilicity are exposed to a humid environment. The hydrophilicity pattern at the surface acts as a template for the formation and growth of liquid droplets or liquid microchannels. All these experiments rely on the availability of defined surfaces consisting of patches of a known size and surface energy. A particularly appealing approach consists in a deliberate functionalization of a surface with monolayers containing molecules which photoreactive moieties. The molecular structure or conformation is changed by light, which in turn yields different macroscopic properties. The desired performance can be achieved by a surface functionalization with azobenzene containing short fluorinated alkyl chains. We could clarify the underlying mechanism. The decisive parameter is the change in the vertical projection of the dipole moment, and other mechanisms such as orientational changes within the functional units can be ruled out. With this knowledge we are now able to predict guidelines for efficient molecular structures.

Nonlinear Optical Devices:

(Collaboration with University of Potsdam,

S. Schrader and the University of Göteborg)

Nonlinear optical devices such as frequency doubler or opto-opto switch based on cascading of $\chi(2)$ -effects are governed by the same figure of merit. Efficient structures require a waveguide format with a high and uniform polar order of the NLO chromophores. Up til now, this was mainly achieved by LB-films or poled polymers with known disadvantages (stability, dilution, preparation). A good review is the following book chapter:

Motschmann, H. and Möhwald, H.: Langmuir Blodgett Films. In: Handbook of Applied Colloid and Surface Chemistry, edited by Krister Holmberg, John Wiley & Sons (2001).

We could achieve the desired structures with ferroelectric liquid crystals (FLC). Usually, liquid crystals possess only an intrinsic quadrupolar order; however, FLC allow also a dipolar order perpendicular to the director. By means of an electric field, it is possible to unwind the adopted helical order of chiral FLC and freeze this arrangement by a polymerization. No defects are induced and a low optical loss is recorded. True phase matching was achieved between fundamental and first order mode using the modal dispersion

of the waveguide. The overlap integral could be maximized by a structural inversion leading to an inversion of the sign of the susceptibility at the nodal plane of the first order mode. We could also demonstrate the potential of cascading nonlinear optical processes for the design of an opto-opto switch which is continued in a DFG-project.

Soluble Surfactants

Soluble surfactants are important for controlling the interfacial properties of liquid-liquid or liquid-air interfaces. They are related to the insoluble monolayers: for instance we have been able to prove the existence of a first order phase transition between a gaseous and a liquid expanded surface phase.

The experimental investigation is complicated due to the low number density within the adsorption layer and the existence of dissolved soluble surfactants in the bulk. Nonlinear optical techniques such as Second Harmonic Generation (SHG) or Sum Frequency Generation spectroscopy are powerful tools for the investigation of these systems. Due to the prevailing symmetry, the signal is only generated within the interface with negligible contribution from the bulk. These features have been used in the past to investigate certain equilibrium of adsorption layers of soluble surfactants such as the odd-even effects in monolayer or the ion distribution at an interface. The aim of this work is to get a better understanding of the interfacial architecture and to shed some light in the relation between molecular quantities and macroscopic quantities. A nice review about these activities can be found in the following book chapter:

Motschmann, H. and Teppner, R.: In Novel methods to Study Interfacial Layers, edited by R. Miller, D. Moebius, Elsevier (2001).

We have now a variety of well characterized model systems which are optimized for the requirement of the nonlinear optical techniques. Our current interest is focused on the investigation of dynamic properties in these systems. This work is done in close collaboration with the group of Dieter Wantke, (Max Planck Institute of Colloids and Interfaces). The major experimental tool in the Wantke group is the oscillating bubble which allows the determination of the surface dilational viscosity and elasticity. Results show in certain circumstances striking deviations from the prediction of the Lucassen van Tempel model. In order to gain further insights we developed a novel version of the oscillating bubble which can be combined with the nonlinear optical techniques. The experimental task turned out to be quite tricky as the laser pulses have to be synchronized with the state of the bubble.

The nonlinear optical set-up probes different interfacial properties as the pressure sensor. The contributions from surface concentration and surface viscosity can be discriminated to allow assessing the disputed intrinsic dilatational viscosity. Furthermore the net exchange rate between bulk and sublayer can be determined.

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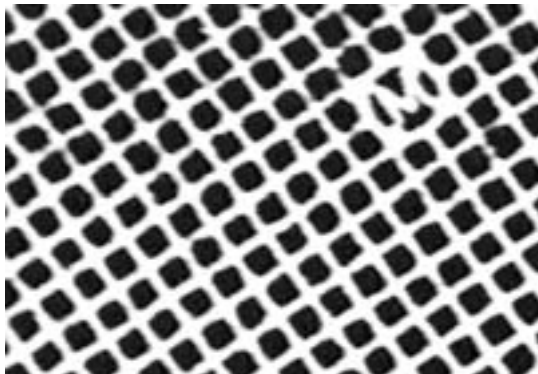


Fig. 1: Wetting pattern generated by a cis-trans motif within a monolayer. The writing process is fully reversible.

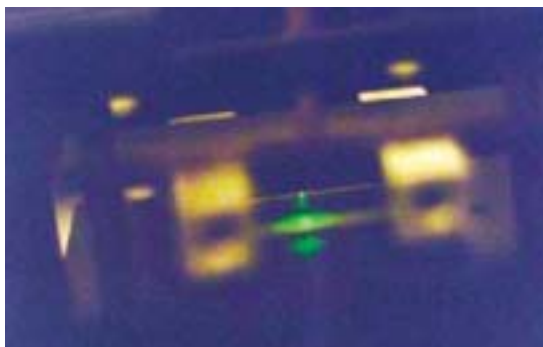


Fig. 2: Efficient conversion in a slab waveguide with an inverted waveguide structure. For the switching experiment the device is operated close to phase mismatch

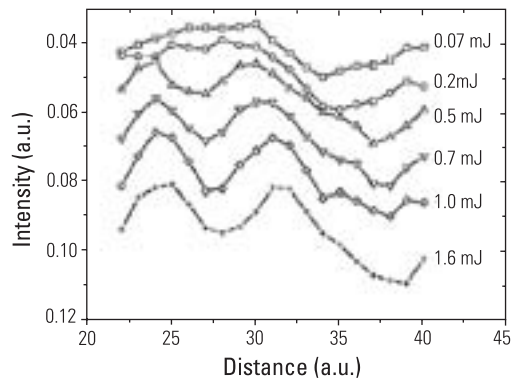


Fig. 3: Interference fringes measured in a MZ interferometer with the inverted waveguide structure in one arm. This experiment yields the nonlinear phase shift.

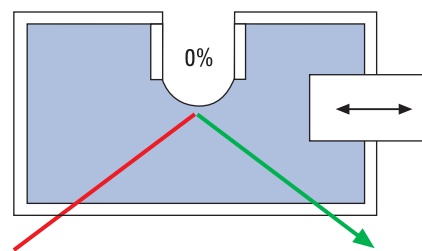


Fig. 4: Oscillating bubble combined with SHG in total reflection mode

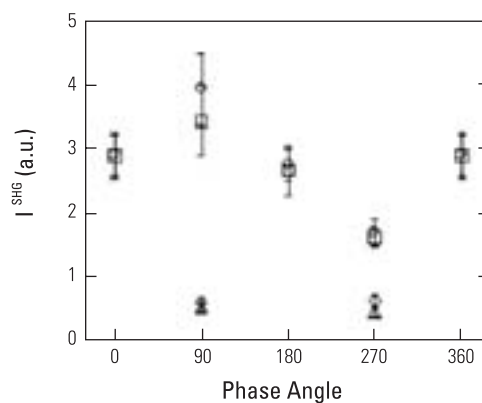


Fig. 5: SHG response as a function of the phase difference between bubble and laser light system

Key Publications:

[1] Radüge, C., Papastavrou, G., Kurth, D. G. and Motschmann, H.: Controlling Wettability by Light: Illuminating the Molecular Mechanism. EPJ E-Soft Matter (in press).

[2] Fluoraru, C., Schrader, S., Dietzel, B. and Motschmann, H.: Phase matched second harmonic generation and cascaded nonlinearity in an inverted waveguide of 2-docosylamino-5-nitropyridine, Journal of Applied Physics 90, 5469 (2001).

[3] Motschmann, H., Lunkenheimer, K.: Phase transition in an Adsorption layer of a soluble surfactant at the air-water surface. Colloid and Interface Science, 248, 462-466 (2002).

Thin Liquid Films



Aims:

The interactions between the interfaces in thin liquid films, for example foam films, significantly influence the properties of adsorbed monolayers of a surfactant at the film interfaces. The stability and the permeability of the film for gases are such quantities depending on the free film interaction energy. We are trying to quantify these dependencies and to give a theoretical description of these effects. Beside this dependence, the gas permeability of foam films is an interesting quantity for itself. We aim to evaluate the influence of physical parameters and structural components of different surfactants for an improved understanding of the permeation mechanism.

Results:

We have found recently that thinning a foam film against repulsive forces in the film causes desorption of a part of the adsorbed surfactant molecules from the film surfaces. On the other hand the density of adsorbed molecules increases, if the film thins spontaneously under the effect of attractive forces. This change of adsorption density causes an increase of gas permeability of the film in the first and a decreasing permeability in the second case [Krustev, R. and Müller, H.-J.: Effect of free energy on the gas permeability of foam films. *Langmuir* 15, 2134-2141 (1999)].

The same mechanism should influence the stability of the films. A theory has been developed for the rupture of foam films on application of external pressure. Very thin foam films, made from a solution with sufficient surfactant can be nearly infinitely stable after reaching their equilibrium thickness. However, if in the "pressure balance experiment" an external pressure acts on the film surfaces in excess to the pressure in the bulk phase of the film forming solution, the film ruptures at a critical pressure. It is known that foam films rupture by a nucleation of holes mechanism, if the density of the adsorbed surfactant molecules decreases under a critical level [Kashchiev, D. and Exerowa, D.: Nucleation mechanism of Newtonian black films. I. Theory. *J. Colloid Interface Sci.* 77, 501-511 (1980)]. Usually the adsorption density is considered as a function of the surfactant concentration in the bulk of the solution. However, in the case of application of pressure the adsorption density is a function of the external pressure too. This is a consequence of the increase of the chemical potential of the surfactant molecules in the film surfaces with increasing pressure. The variation of the adsorption density with pressure can be calculated by our concept of "enhanced colloidal interaction". Without additional pressure the adsorption density Γ_f is high and the film is stable. With increasing pressure Γ_f decreases. If Γ_f becomes equal or smaller than the critical value Γ_c the film will rupture (Fig. 1). This model should be applicable also for the stability of emulsions under osmotic stress or in a centrifuge.

The measurement of the gas permeability is a sensitive tool to detect changes in the structure of the foam film. In the investigation of the permeability of foam films stabilized with different surfactants we found that very thin bilayer foam films from n-dodecyl- β -D maltoside exhibit the smallest permeability among different ionic and non-ionic surfactants investigated in our lab. Films with this surfactant also show a distinct minimum of the permeability on variation of the temperature at 25 °C. This behavior deviates from that of other non-ionic surfactants, where the permeability increases monotonously with temperature in the investigated range from 15 to 35 °C.

An interesting new aspect of the mechanism of gas permeation through foam films has been found in the investigation of foam films stabilized with a series of non-ionic oxethylated dodecanol surfactants ($C_{12}E_n$). Here the permeability clearly depends on the size of the headgroup (Fig. 2). For many other surfactants the permeability can be described sufficiently correct by a three layer model with two covering layers of the alkyl chains of the surfactant and an aqueous core including the surfactant headgroups. In the case of surfactants of the type $C_{12}E_n$ the headgroups are larger and may form a gel-like layer with a smaller diffusion coefficient than that in water. The dependence of the permeability on the number of EO-groups in the surfactant molecule can be rationalized by taking into account that the thickness of this gel-like headgroup layer is proportional to the square root of n for $n \geq 9$ and decays faster for n decreasing below 9.

As mentioned above it has been shown that on the one hand the free film interaction energy affects the density of the adsorbed surfactant molecules in the surfaces of the film, which on the other hand influences important film properties as stability and permeability. The free interaction energy can be determined by measurements of the disjoining pressure isotherms or the contact angle between the film and the surrounding meniscus of the bulk liquid. Fig. 3 shows disjoining pressure isotherms of the anionic surfactant tetraethyl ammonium perfluoro octane sulphonate. The integral over the isotherm yields the interaction free energy. The graph for 0.0005 M NH_4Cl shows a slight increase of the gradient with decreasing thickness of the film. Such behavior is an indication of a dependence of the strength of the interaction on surfactant concentration and of a variation of the adsorption density. Measurements of contact angles of foam films stabilized with ionic surfactants give more and stronger indications for such a dependence, which is not taken into account in the classical DLVO-theory and has not been investigated systematically until now.

Hans-Joachim Müller 11.02.39

1967: Diploma, Physics

(Humboldt-Universität zu Berlin)

Thesis: Pulsed gas ion laser

1972: PhD, Physics (Institute of Optics and Spectroscopy of the Academy of Sciences of the GDR, Berlin) Thesis: Pulsed laser action in metal vapors

1971-1978: Research Scientist (Institute of Organic Chemistry of the Academy of Sciences, Berlin)

1979-1991: Group Leader

(Institute of Organic Chemistry of the Academy of Sciences of the GDR, Berlin)

Since 1992: Group Leader

(Max Planck Institute of Colloids and Interfaces, Golm)

In the investigation of the permeation of different gases through foam films (O_2 , N_2 , Ar) it has been found that the differences in the permeability are of the same order as for typical gas separation polymer membranes. A concept for supported foam film membranes has been developed based on our experimental results. The foam films are formed in the pores of a porous body. The favorable properties of foam films as self-organization, high gas flux per unit of area and switchability may become accessible for technical application in this way.

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Key Publications:

[1] Brezesinski, G., Müller, H. J., Toca-Herrera, J. L., Krustev, R.: X-ray diffraction and foam film investigations of PC-headgroup interaction in water/ethanol mixtures. *Chemistry and Physics of Lipids* 110, 83-194 (2001).

[2] Krustev, R., Müller, H. J.: An apparatus for the measurement of the gas permeability of foam films. *Rev. Scient. Instr.* 73, 398-403 (2002).

[3] Muruganathan, R. M., Krustev, R., Ikeda, N., Müller, H. J.: Temperature dependence of the gas permeability of foam films stabilized by dodecyl maltoside. *Langmuir* 19, 3062-3065 (2003).

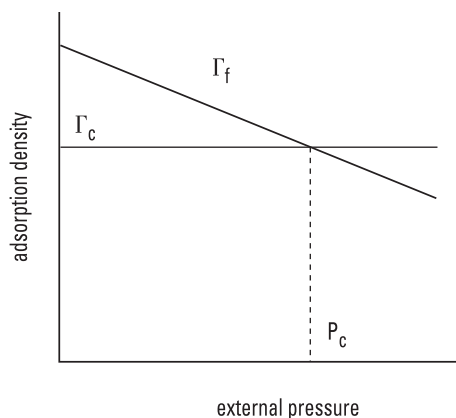


Fig. 1: Foam film rupture at a critical pressure p_c

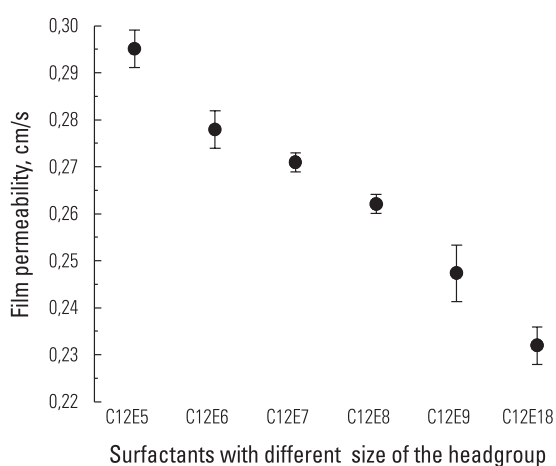


Fig. 2: Gas-permeability of foam films depending on the number of EO-groups in the stabilizing oxethylated dodecanole

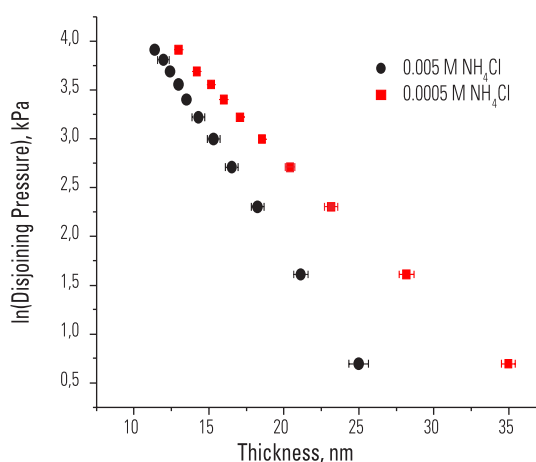


Fig. 3: Disjoining pressure of a perfluoro octane surfactant as a function of film thickness for different concentrations of NH_4Cl

Supramolecular Organization of Amphiphilic Monolayers



Aims:

- 1) Molecular recognition of dissolved pyrimidine derivatives by medium-chain dialkyl Melamine Type Monolayers (with F. Liu and S. Siegel)
- 2) Phase transition in monolayers (with S. Siegel and in cooperation with V. B. Fainerman and Yu. B. Vysotsky, Ukraine)
- 3) Molecular chirality and the morphology of biomimetic monolayers (with N. Nandi, India)
- 4) A new phenomenon: Auto-oscillation of surface tension (with O. Grigorieva and in cooperation with N. M. Kovalchuk and V. I. Kovalchuk, Ukraine)

Results:

1) Amphiphilic "host-guest" assemblies with highly specific surface textures have been formed between a monolayer and surface-inactive "guest" molecules dissolved in the aqueous subphase. Melamine-type amphiphiles have been synthesized, which are good candidates for molecular recognition of pyrimidine derivatives. Whereas the melamine type monolayers form non-textured condensed phases on the pure aqueous subphase, highly specific, complicated shapes and inner textures of the condensed phase are formed if uracil, thymine or barbituric acid are dissolved in the aqueous subphase. This is demonstrated by **Fig. 1** with some characteristics of diundecyl ($\text{CH}_3(\text{CH}_2)_{10}_2$ melamine type [2,4-di(n-undecyl-amino)-6-amino-1,3,5-triazine] monolayers spread on 0.1 mM thymine solution at 27 °C. Already at zero pressure dumb-bell shaped domains with specific variation of the inner texture are formed (see BAM images of **Fig. 1**). The GIXD studies show only quantitative changes in the rectangular lattice structure by molecular recognition of thymine (see contour plots of **Fig. 1** at $T = 20$ °C).

2) OH- substitution in different (2-, 9-, 11-, 12-) positions of the alkyl chain affects strongly and in different way both the phase behavior and the domain texture of the non-substituted fatty (palmitic, stearic) acid monolayers. Striking shape changes with temperature of the condensed phase domains are observed and demonstrated for 9-hydroxypalmitic acid in **Fig. 2**.

9-OH and 11-OH substituted stearic acid monolayers have rectangular lattices with tilt towards the NNN direction, whereas 12-OH stearic acid has an oblique lattice over the whole pressure range.

The following theoretical work has been performed:

- Development of a model for the kinetics of 2D condensation of Langmuir monolayers which accounts for different mechanisms of monomer aggregation and different dependencies of the aggregation rate on time.
- Derivation of new equations of state for mixed monolayers of an insoluble and a soluble homologue and of the adsorption isotherm equation for soluble amphiphiles which reflects well the experimental results.
- Comparative analysis of theoretical models, which describe the displacement of the 2D phase equilibrium in monolayers. A model for the temperature dependence of the main phase transition is developed which takes into account the presence of solvent and monolayer compressibility.

- Quantum chemical analysis (PM3 approximation) of the thermodynamics of the 2D-cluster formation of fatty alcohols (even/odd effect and 2-methyl substitution). Enthalpie, Entropie and Gibbs energy for the formation of defined small associates are calculated and an additive approach is developed to extend the calculations to infinite clusters. Good agreement with the results of our thermodynamic models is obtained.

3) A large variety of chiral discrimination effects have been observed in monolayers with several amino acid amphiphiles and phospholipids using BAM, GIXD and also surface pressure measurements. One lacuna of the studies of chirality effects in monolayers is the large gap between the experimental observation and the theoretical understanding. We correlated the chiral molecular structure of the above amphiphiles and the handedness of the mesoscopic domain using an effective pair potential (EPP) theory. In the case of DPPC, the neighboring molecular directors are in a mutually oriented state along the width and length of the arms of the triskelion (**Fig. 3**).

The studies use a coarse-grained description of the molecule and calculate the pair potential between a pair of molecules without using any adjustable parameter. The calculated pair potential indicates that chiral molecules can be arranged starting from a reference molecule in a successive way leading to a stable aggregate only if the molecules mutually orient in a specific direction characteristic of the enantiomer. The orientation of molecules in opposite direction is unfavorable. This explains the high specificity of the chiral interactions in determining the aggregate curvature at molecular level. The chirality at the lower level of structure hierarchy affects the chirality at a higher level in biomimetic systems.

4) Auto-oscillations of surface tension develop in systems where a surfactant droplet is situated at the tip of a capillary under a free liquid surface. This system represents the simplest non-linear oscillation system known so far. **Fig. 4** shows the characteristic oscillations of octanol.

The experimental observations show that the characteristics of the surface tension auto-oscillations depend on the surfactant properties and the system geometry. A new mathematical model reflects correctly the main regularities of the system evolution observed in the experiments, e.g. relationship between oscillation behavior and system geometry (**Fig. 5**).

The main driving force for the development of auto-oscillations is the surface tension gradient (Marangoni effect). The auto-oscillation is a result of instability arising and fading in the system that leads to interchange of convective (fast) and diffusive (slow) stages in the system evolution.

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Dieter Vollhardt 26.08.1937

1961: Diploma, Chemistry
(University of Greifswald)

Thesis: Effect of the glassy and microcrystalline state on the fluorescence behaviour

1966: PhD, Physical Chemistry

(Humboldt-University Berlin)
Thesis: Desorption studies of surfactants using a new diffusion-kinetic system

1966-1971: Group Leader

(Institute of Fatty Chemistry of the German Academy of Science)

1972-1991: Group Leader (Central Institute of Organic Chemistry of the Academy of Science)

1982: Habilitation

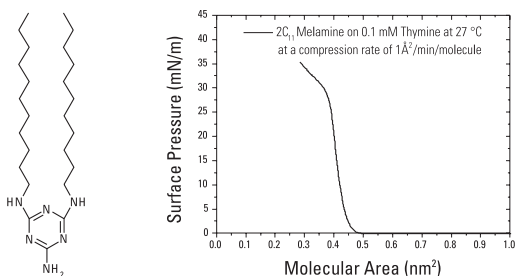
(Academy of Sciences, Berlin)
Thesis: Studies of structure and molecular interactions in amphiphilic monolayers at the air/water interface

1992: Group Leader

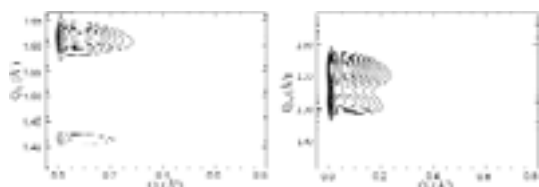
(Max Planck Institute of Colloids and Interfaces, Golm)

1999: Professor

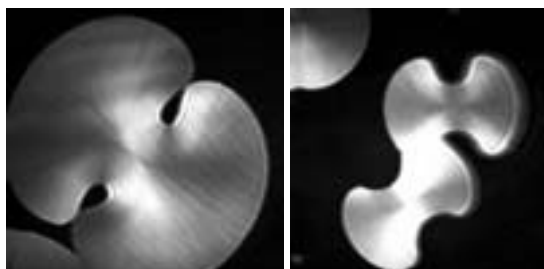
(University of Potsdam)



Formula and π -A isotherm



Grazing incidence X-ray diffraction (GIXD): Contour plots on water (left) and on 0.1 M thymine (right); $T = 20^\circ\text{C}$



Brewster Angle Microscopy (BAM) images at 0.63 (left) and 0.53 $\text{nm}^2/\text{molecule}$ (right)

Fig. 1: Molecular recognition of dissolved thymine

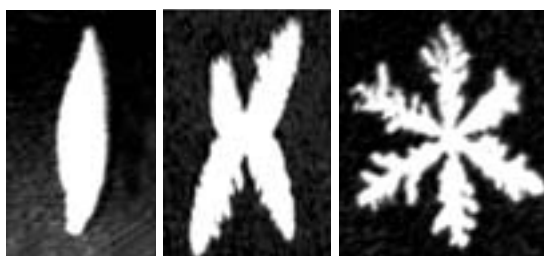


Fig. 2: Representative domains of 9-hydroxy-palmitic acid monolayers at 5, 10 and 15°C

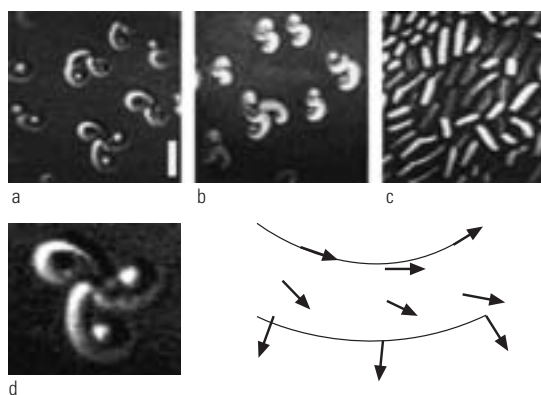


Fig. 3: BAM images of (a) D- (b) L- and (c) DL-DPPC domains; an enlarged D-DPPC domain in (d), and changes in molecular director within an arm of the triskelion in (e)

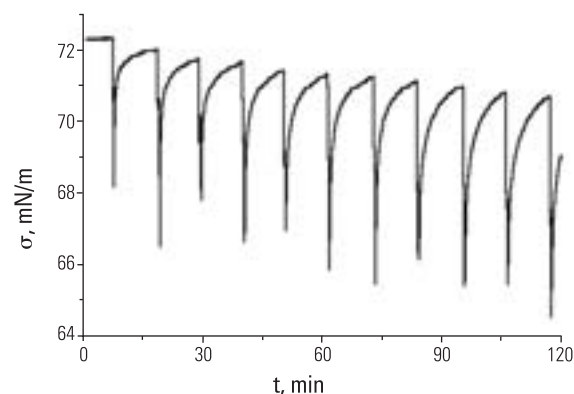


Fig. 4: Surface tension σ versus time, Auto-oscillation in octanol-water system, 9 mm capillary immersion depth; 46 mm cell diameter

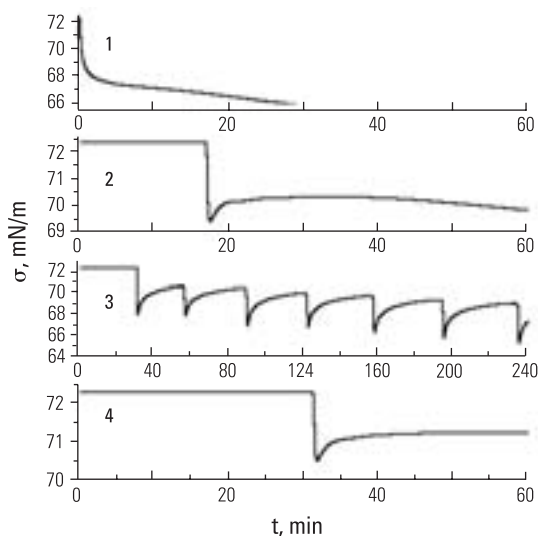


Fig. 5: Surface tension σ versus time. Oscillation behavior in dependence on system geometry. Constant cell diameter of 40 mm (1-3) and larger (60 mm) (4); immersion depth is small (1 mm) (1), medium (6 mm) (2), large (8 mm) (3) (4).

Key Publications:

[1] Vollhardt, D.: Morphology of Monolayers at Air/Water Interfaces. in: Encyclopedia of Surface and Colloid Science, Ed. A. Hubbard, Marcel Dekker, New York, 2002, 3585-3601.

[2] Kovalchuk, N. M. and Vollhardt, D.: Theoretical description of repeated surface-tension auto-oscillations. Phys. Rev. E 66, 026302-1-9 (2002).

Rheological Properties of Fluid Interfaces



Aims:

- Understanding rheological properties of fluid surfaces and interfaces and their influence on the stability of complex systems like foams and emulsions
- Assessing the influence of molecular exchange processes on surface rheological properties
- Development of a framework for the uniform description of inhomogeneous fluid structures

Results:

In previous work it was demonstrated that surface dilatational moduli of surface active solutions measured with the oscillating bubble method show different characteristic forms due to various rheological effects. For example, a few solutions exhibit the influence of an intrinsic surface dilatational viscosity which stabilized foams [1]. After the systematic investigation of unmixed surfactant solutions the rheological measurements were focused on mixed solutions in the last years. Characteristic examples are solutions of SDS/dodecanol and polyelectrolyte/surfactant mixtures. Their surface dilatational moduli reflect the specific influence of the components on the surface rheology. A SDS solution without added dodecanol has a distinct intrinsic dilatational surface viscosity combined with an effect due to the bulk diffusion, whereas, an increasing amount of added dodecanol causes more and more elastic surfaces (Fig. 1). The higher surface activity of dodecanol explains the slow replacement of the SDS molecules at the surface which is detectable by the change of the modulus in time. Other results demonstrate that the modulus can be also used for the characterization of the interaction between polyelectrolyte and surfactants. For example, a pure gelatin solution has a purely elastic surface, whereas, surfaces of gelatin/sodium sulfosuccinate solutions are strongly viscoelastic. In addition, it could be demonstrated by other measurements that the intrinsic dilatational surface viscosity of such mixtures stabilizes not only foams but also high speed coating processes in the silver halide photographic industry [2].

For the explanation of the frequency characteristics of surface dilatational moduli a model was introduced which is based on molecular exchange processes between the surface monolayer and the adjacent bulk phase. This exchange leads in a nonequilibrium state to a dissipative loss that means, to a viscous effect. The fit of a measured surface dilatational modulus as a function of frequency using this model yields information about the dynamic surface tension, the influence

of the bulk diffusion, the elastic and viscous properties of the surface, the change in monolayer and sublayer concentrations during the oscillations, the molecular exchange rate and the related dissipative loss. The evaluation of our comprehensive experimental material led to a few new questions. In some concentration ranges the change in the monolayer concentration and its influence on the modulus show unexpected behavior. The effects are too small near the CMC and too large in the low concentration range. For the verification of these effects an independent experiment was proposed and realized in cooperation with the group of H. Motschmann. Using this new set up the monolayer concentration at an oscillating bubble can be monitored instantaneously in different position with a pulsed Laser due to the SHG effect. First results with solutions of a fluorochemical-based surfactant show the predicted behavior (J. Örtengren, H. Motschmann). The average and the relative change in monolayer concentrations monitored at an oscillating bubble with SHG light correspond to the mentioned surface rheological effects. Both experiments demonstrate that in the low concentration range the dynamic surface tension is only a function of the monolayer concentration, whereas, the sublayer has a direct influence near the CMC.

Another focus of the group was in the last years the theoretical interpretation of experiments using a chemical force apparatus with prepared tips and samples. The experiments were carried out by G. Papastavrou (Universität Greifswald). Adhesion experiments were evaluated with a semi-empirical model (P. Warszynski/Krakau) and described in the framework of general multidimensional classical field. A similar interpretation was given for friction experiments and supported by a few numerical calculations. In addition, specific interaction and summation rules for the components of such complex systems were defined according to the principles of electromagnetic interaction [3].

Aims of the group in the next years are further the detailed investigation of molecular exchange processes at a fluid surface or interface and their influence on rheological properties. In particular, the explanation of the origin of the intrinsic surface viscosity requires more information about this molecular exchange mechanism and the related dissipative loss. For this reason further surface rheological and optical (SHG) measurements are planned. In addition, the results should be compared with properties of complex systems like foams.

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Klaus-Dieter Wantke 08.12.1940

1964: Diploma, Physics (Martin-Luther-Universität Halle-Wittenberg)

Thesis: Berechnung eines unstationären Eigenspannungsproblems

1971: PhD, Physics (Martin-Luther-Universität Halle-Wittenberg)

Thesis: Ein Näherungsverfahren zur Lösung von Spaltbeugungsproblemen

1964-1988: Collaborator (Institute of Telecommunication of the East-German Post, Berlin-Adlershof)

1989-1991: Scientific Collaborator (Institute of Organic Chemistry, Academy of Science, Berlin-Adlershof)

Since 1992: Group Leader (Max Planck Institute of Colloids and Interfaces, Berlin-Adlershof/Golm)

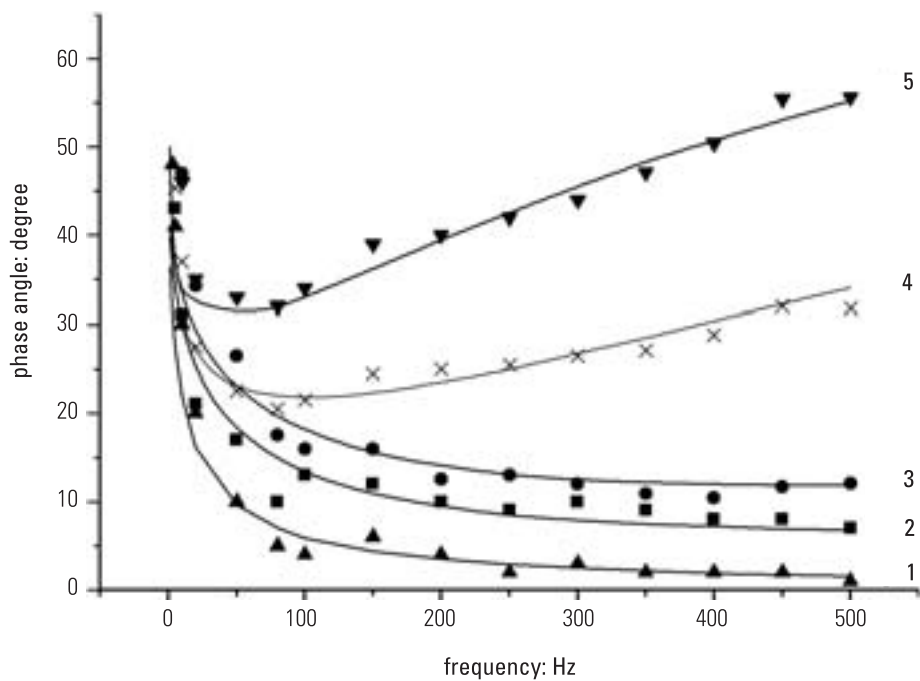
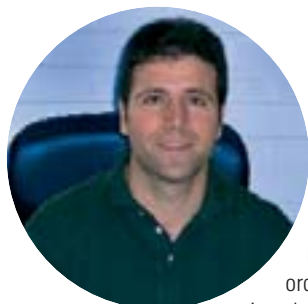


Fig 1: Phase angle of the surface dilatational modulus as a function of frequency for mixed $5 \cdot 10^{-3}$ M SDS/x mol% dodecanol solutions: (1/ ▲) x=0.4 mol% ($f > 100$ Hz: pure elastic surface), (2/ ■) x=0.1 mol%, (3/ ●) x=0.06 mol%, (4/ ×) x=0.05 mol%, (5/ ▼) x=0 mol% (viscoelastic surfaces), (—) theoretical curves.

Key Publications:

- [1] Wantke, K.-D. and Fruhner, H.: Determination of Surface Dilational Viscosity Using the Oscillating Bubble Method, *J. Colloid Interface Sci.* 237, 185-199 (2001).
- [2] Fruhner, H. and Wantke, K.-D.: The role of surface viscoelasticity in slide coating processes, *Colloid Polymer Sci.* 279, 898-908 (2001).
- [3] Warszynski, P., Papastavrou, G. Wantke, K.-D., Möhwald, H.: Interpretation of adhesion force between self-assembled monolayers measured by chemical force microscopy, *Colloids Surfaces A* 214, 61-75 (2003).

Nanostructured Interfaces and Materials



Aims:

The principal activities of the group involve the nanoscale surface functionalization of colloid particles and macroscopic supports through self-assembly. We concentrate on manipulating colloidal interactions, primarily between a host of colloids and polymers, in order to selectively modify and stabilize particles in solution, and to drive their assembly onto surfaces

to construct nanostructured, functional materials. Since much of our research is concerned with polyelectrolyte-mediated adsorption, we are also focusing on developing a fundamental knowledge of the factors governing the adsorption behavior of a variety of charged polymers. The interface-engineered materials prepared have applications in catalysis, sensing, separations, coatings, and pharmaceuticals.

Results:

A. Preparation of Tailored, Functional Colloids

By exploiting the electrostatic, consecutive self-assembly of a broad class of species onto various colloid particles, coated colloids with diverse compositions and function were prepared. The colloid cores, comprised of polymeric, inorganic or biomaterials, exhibited shapes from spheres to high-aspect ratio rods, and spanned the micrometer to nanometer size range. The coating layers included functional (conducting and luminescent) and cross-linkable polymers, various nanoparticles (silica, iron oxides, zeolites, titanium dioxide, and gold), biomacromolecules (e.g., proteins and enzymes), or dendrimers. These coated colloids offer new perspectives for advanced materials preparation since they often exhibit enhanced and novel properties when compared with their single component particles. Several examples are highlighted in the following.

(i) Biocolloids.

Colloidal biocatalysts, comprising magnetic-functionalized polymer carrier particles coated with enzyme (glucose oxidase, horseradish peroxidase, or urease) multilayers were prepared. These high surface area colloids were successfully exploited as specific enzyme reactors. It was demonstrated that the enzymatic activity per particle could be tailored, depending on the number of enzyme layers immobilized. Our related work using protein-functionalized, fluorescent particles showed that they could be successfully employed in solid-phase assays, providing similar sensitivity to existing commercial immunoassays.

(ii) Nanoparticle Functionalization.

By taking into account the polymer length, polymer stiffness and added salt concentration, as well as nanoparticle curvature influences, suitable conditions that are in agreement with theoretical predictions (e.g., a polymer Mw of about 15-20 kDa and 1 mM salt solutions), were established to deposit polyelectrolyte multilayers on gold nanoparticles (**Fig. 1**). Red shifts in the spectral position of the surface plasmon absorption band peak of the gold nanoparticles were observed, confirming the uniform deposition of the multilayers. Our recent studies show that sub-10 nm diameter gold particles can also be coated with polyelectrolyte layers. The attachment of proteins onto polyelectrolyte-coated gold nanoparticles has also been achieved for their utilization in biolabeling.

(iii) Gold-Coated Spheres.

Densely packed metal nanoparticle coatings were prepared on submicron-sized latex spheres (**Fig. 2**). This was made possible by using gold nanoparticles with different surface characteristics; e.g., silica-encapsulated gold nanoparticles (Au@SiO₂) and gold nanoparticles stabilized by 4-dimethylamino-pyridine. The surface properties of these particles were exploited for the formation of close-packed nanoparticle assemblies onto larger spheres. A recent advance was also made by self-assembling oligosilsesquioxane-capped silver nanoparticles, which also yielded dense nanoparticle layers on larger particles. These metal-shell particles represent a new class of colloids with optical properties that can be tailored by changing the hierarchical assembly of the nanoparticles.

B. Advanced Materials from Coated Colloids

(i) Colloidal Crystals. We have demonstrated the use of coated colloids for the formation of colloidal crystals. Coatings comprising pure polyelectrolyte, semiconductor nanoparticle/polyelectrolyte, and gold nanoparticle/polyelectrolyte multilayers were formed on submicrometer-sized polystyrene spheres, and the resulting coated colloids were assembled into ordered arrays (**Fig. 3**). The position of the optical stop band of colloidal crystals of coated colloids could be tuned with nanoscale precision through variation of the coating thickness and/or the composition of the coating.

(ii) Macroporous Materials.

Macroporous titania and inorganic-composite structures were produced by infiltrating a titanium dioxide precursor into templates of sedimented, close-packed coated colloid spheres, followed by removal of the organic material by calcination. The pore morphology (open or closed) of the resulting macroporous structures was controlled by the nature of the multilayers, and the wall thickness of the pores was tuned on the nanometer scale by varying the number of deposited multilayers. A variety of composite inverse opals were also prepared from colloidal crystals made from polyelectrolyte-coated particles.

Frank Caruso 01.01.1968

1989: B. Sc. (Hon.),

Physical Chemistry (The University of Melbourne, Australia)

Thesis: A Fluorescence Study of Lateral Diffusion Coefficients in Phospholipid Monolayers at the Air-Water Interface

1994: Ph.D., Physical Chemistry

(The University of Melbourne, Australia)

Thesis: Lateral Diffusion of Amphiphiles in Air-Water Monolayers and Langmuir-Blodgett Films

1994-1996: Postdoctoral Fellow,

Division of Chemicals and Polymers (CSIRO, Melbourne, Australia)

1997-1998: Alexander von Humboldt Research Fellow (Max Planck Institute of Colloids and Interfaces, Golm)

1999-2002: Group Leader

(Max Planck Institute of Colloids and Interfaces, Golm)

Since 2003: Professor, Department of Chemical and Biomolecular Engineering (The University of Melbourne, Australia)

(iii) Biocatalytic Films.

Polyelectrolyte-enveloped enzyme crystals were alternately assembled on planar supports with an oppositely charged polymer to create multilayered thin films for biocatalysis applications. Thin films of controllable thickness and biocomponent content, both tunable by the number of layers deposited and the original size of the biocrystal template were fabricated. These enzyme multilayer films were stable, relatively thin (several micrometers), and contained a high enzyme content. They displayed biocatalytic activities of up to fifty times higher than those prepared by the consecutive deposition of solubilized enzyme and polyelectrolyte.

C. Multilayered Thin Films

Thin films of weak polyelectrolytes and copolymer/polyelectrolyte multilayers were prepared on both planar and spherical (colloid) supports to investigate the role and extent of electrostatic interactions in polymer films. Weak polyelectrolyte multilayer films of poly(acrylic acid) and poly(allylaminehydrochloride) (PAH) were formed on particles under optimized pH conditions, and the coated colloids were found to be colloidally stable. Diallyldimethylammoniumchloride-based copolymers with varying charge density showed the existence of a critical charge density limit between 75% and 53%, below which no significant layer growth was possible when assembled in alternation with PSS. Dendrimer-based polyelectrolyte multilayer films were also prepared and shown to be suitable ultrathin nanoreservoirs for the loading and controlled release of various drug substances. The amount of loaded drug as well as the drug release properties could be readily modulated through variation of the film processing parameters and film composition.

F. Caruso, T. Cassagneau, J. Cho, D. Gittins, W. Jin, N. Kato, A. Khopade, G. Kumaraswamy, Z. Liang, K. S. Mayya, F. Meiser, C. Pilz, B. Schöler, C. Schüler, P. Schütz, X. Shi, A. Susha, D. Wang, A. Yu
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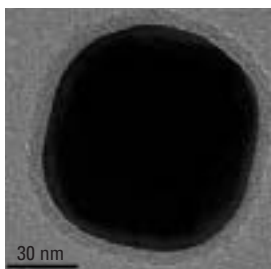


Fig. 1.: TEM micrograph of a gold nanoparticle coated with two layers of oppositely charged polyelectrolytes.

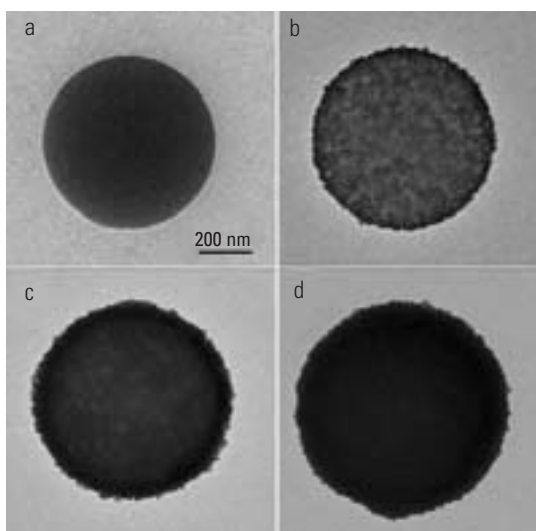


Fig. 2.: TEM micrographs of (a) a two-layer polyelectrolyte-coated polystyrene sphere and identical spheres additionally coated with (b) one, (c) three, and (d) five Au@SiO₂ nanoparticle/polyelectrolyte bilayers.

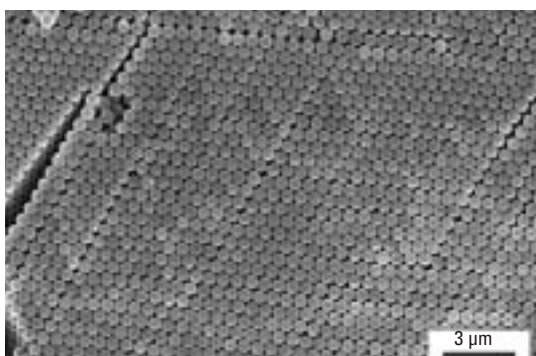


Fig. 3.: SEM image of a colloidal crystal made of polystyrene particles coated with a total of six poly(allylaminehydrochloride)/poly(styrene sulfonate) layers.

Key Publications:

- [1] Gittins, D. I. and Caruso, F.: Tailoring the Polymer Coating of Gold Nanoparticles, *J. Phys. Chem. B* 105, 6846 (2001).
- [2] Jin, W., Shi, X. and Caruso, F.: High Activity Enzyme Microcrystal Multilayer Films, *J. Am. Chem. Soc.* 123, 8121 (2001).
- [3] Liang, Z., Susha, A. S., and Caruso, F.: Metalodielectric Opals from Layer-by-Layer Processed Coated Colloids, *Adv. Mater.* 14, 1160 (2002).

NON-PLANAR INTERFACES

Mechanics and Adhesion of Capsules and Strongly Deformable Colloids



Aims:

In recent years much attention has been paid to compliant colloids like capsules of colloidal dimensions or microgel-particles. The interest in these systems is stimulated by the numerous applications in which responsive colloids are already used especially in the field of life sciences. Here these colloids are often used as carrier particles protecting and gradually releasing agents. Depending on the particular application, these agents can be drugs (drug delivery), cosmetics or perfumes just to mention some examples. Apart from these technologically relevant examples there are also numerous examples of compliant colloids in nature like bacteria, cells or viruses.

From the point of view of basic science, compliant colloids are interesting because the energy cost for significant shape changes is not orders of magnitude larger than typical (surface) interaction energies as it is the case for stiff particles. Therefore, in order to understand particle-particle or particle-substrate interactions, not only knowledge of the governing surface interactions but also of the deformation characteristics is essential. This opens new possibilities to determine the behaviour of particles on surfaces not only by controlling their surface properties but also by controlling their mechanical properties.

In this context hollow shells made from polyelectrolyte multilayers are an interesting model system: These shells are produced by stepwise coating of massive particles and subsequent dissolution of the particle. The original coating remains as a freestanding hollow capsule whose thickness is set by the number of coating cycles. Under suitable conditions, the thickness increase per coating cycle is constant and can be as small as 1-2 nm. The deformability of the system is depending on the total thickness of the capsule-wall and by the materials forming the coating. Thus the deformability can be varied by using different materials for the coating and by using a different number of coating cycles for a given material. At the same time, the surface interactions are determined by the last layer of the coating. Such, both surface interactions and mechanical properties can be varied independently.

Results:

Measurement of Surface Interactions of Coated Colloids by Colloidal Probe AFM

(V. Bosio; G. Bogdanovic)

While the atomic force microscope (AFM) is still predominantly used for measuring the topography of sample surfaces, it can also be employed for quantifying surface interactions. In the force spectroscopy mode, the AFM is used to measure forces acting on the AFM probe as a function of the distance from a surface. In the colloidal probe technique a colloidal particle of several microns diameter is used as an AFM probe. This has the advantage that the geometry of the particle is well known and perfectly spherical which makes it possible to obtain the dependency of the interaction energy/area on the distance (which is the physically important quantity) from the force-distance data via the Derjaguin relation. This is not possible to do with standard AFM probes that are sharp tips of small and undefined radius of curvature.

We have investigated the interactions of polyelectrolyte multilayer coated particles and identically coated flat surfaces in aqueous environment. Here we could confirm and quantify the electrostatic nature of the interactions and find indeed that the interactions are dominated by the last assembled layer.

Direct Measurement of Capsule Deformability by Combined AFM Force-Spectroscopy and Reflection Interference Contrast Microscopy

(F. Dubreuil, N. Elsner, G. Bogdanovic)

For quantifying the deformation properties of polyelectrolyte capsules, we have combined AFM force spectroscopy with Reflection Interference Contrast microscopy (RICM). The latter technique measures accurately the shape of an object resting on a flat transparent surface by illuminating it with monochromatic light and recording the resulting interference pattern. Thus we can use the AFM to press on capsules with a defined force and monitor simultaneously the deformation response of the capsule. This combination of methods allows checking and refining the models used for the deformability of "soft" colloids. Other than in conventional AFM force-spectroscopy, the deformation of the probe can be directly measured.

For small deformations we find that the capsules behave elastically and we can estimate the Young modulus of the shell material from the force-deformation relation. We find that it strongly depends on the material used for building up the multilayer and varies between 0.1 and 10 GPa. For stronger deformations, buckling of the capsules occurs that is only partially reversible.

See **Fig. 1** for typical changes in the contact geometry of a shell.

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1996: Diploma, Physics

(Universität Konstanz)

Thesis: Measurement of sedimentation velocity of colloids

2000: PhD, Physics

(Max Planck Institute of Colloids and Interfaces, Golm)

Thesis: Scanning Force Microscopy on Liquids and its application for characterizing the wetting behaviour of thin liquid crystalline films

2000/2001: Postdoc

(Institute Curie, Paris)

Since 2001: Group Leader

(Max Planck Institute of Colloids and Interfaces, Golm)

Studying the Impact of PE-Capsule Properties on Their Adhesion Behaviour

(N. Elsner, M. Nolte, J. Heuvingh)

The adhesion-geometry of PE-capsules can be studied with RICM and Fluorescence Microscopy. So far we have focused on adhesion induced by electrostatic interactions on homogeneous substrates. Capsules show strong adhesion on oppositely charged substrates while they are not adhering on equally charged substrates. In the first case, they deform to establish a circular contact disc on the substrate. The size of the contact disc can be controlled by the thickness and the material constituting the capsules: By increasing the capsule thickness or choosing a stiffer material, the deformation energy that is accompanying the development of an adhesion disc is rising and thus the contact area is decreasing. Here we are aiming on developing a quantitative picture of the adhesion process that allows predicting the size of adhesion areas as a function of capsule dimensions and material properties.

Further activities are exploring the possibilities to direct adhesion to certain substrate regions by using patterning of substrates by microcontact printing as well as using receptor-ligand type interactions instead of electrostatic interactions as driving force for the adhesion process (biomimetic adhesion).

A. Fery, G. Bogdanovic, V. Bosio, F. Dubreuil, N. Elsner, J. Heuvingh, M. Nolte
andreas.fery@mpikg-golm.mpg.de

Key Publications:

[1] Fery, A., Puech, P., Moya, S., Brochard-Wyart, F., Möhwald, H.: Interaction of polyelectrolyte coated beads with phospholipid vesicles. Accepted in Comptes Rendus de l'Academie des Sciences.

[2] Kato, N., Schuetz, P., Fery, A., Caruso, F.: Thin Multilayer films of weak polyelectrolytes on colloid particles. *Macromolecules* 35, 9780-9787 (2002).

[3] Fery, A., Scholer, B., Cassagneau, T., Caruso, F.: Nanoporous thin films formed by salt-induced changes in multilayers of poly(acrylic acid) and poly(allylamine) *Langmuir*, 17(13), 3779-3783 (2001).

[4] Baigl, D., Ober, R., Qu, D., Fery, A., Williams, C. E.: Correlation length of hydrophobic polyelectrolyte solutions. (accepted in *Europhysics Letters*).

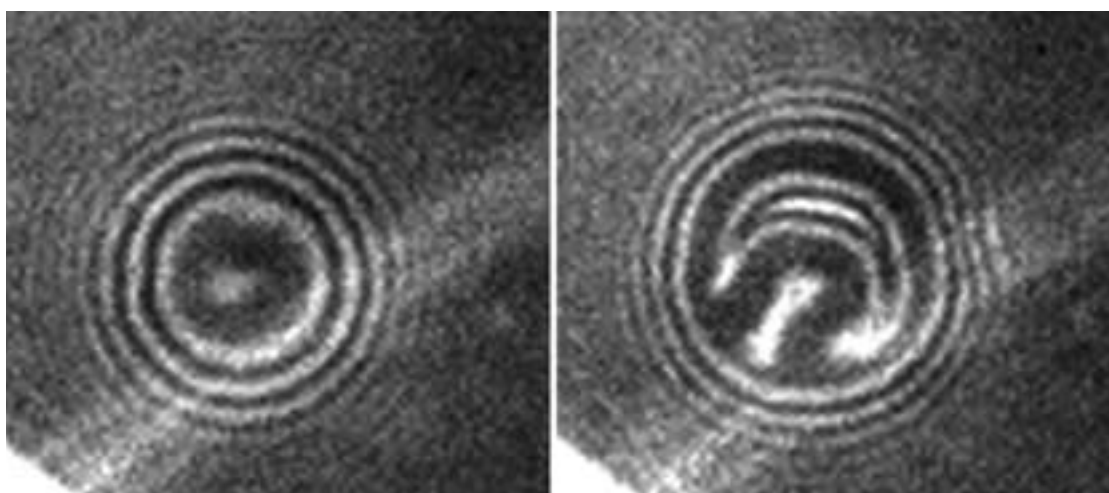


Fig. 1: Interference pattern of a load-free capsule with spherical geometry (left) and the same capsule under load that leads to buckling (right)

NON-PLANAR INTERFACES

Modular Materials: From Dynamic to Nanotechnological Devices



Aims:

Our research integrates all aspects of molecular self-organization as a tool to fabricate materials, devices, and nano-technological systems. Non-covalent interactions are utilized to combine, position, and orient supramolecular modules (SUMOs) in various architectures, including nanostructures, monolayers, thin films, as well as mesophases. A fundamental

goal is to implement stimuli-responsive and intelligent properties in materials. Our research embraces all aspects of structure and property examination in order to establish structure-property relationships of the materials. Two classes of components are relevant for our work, namely metallo-supramolecular assemblies and polyoxometalate clusters (POM). These components possess a wide range of structural and functional properties (electrochemistry, photochemistry, catalysis etc.) that make them potential components for displays, sensors, separation, catalysis, electro-optical and magnetic devices.

Results:

Metallo-Supramolecular Modules (MEMOs)

Discrete metallo-units with aryl moieties, such as pyrene, form arrays on charged surfaces through electrostatic as well as π - π stacking interactions. The films are prepared by subsequent deposition of the positively charged metallo-unit and negatively charged polyelectrolytes, using electrostatic layer-by-layer self-assembly (ELSA). Film growth is linear and the resulting films are very smooth, as shown by X-ray reflectance.

Ditopic ligands based on terpyridine metal ion receptors self-assemble with transition metal ions, such as Fe(II), Ni(II), or Co(II), to metallo-supramolecular polyelectrolytes (MEPEs). The molar mass of MEPE was investigated by analytical ultracentrifugation. We could show that the molar mass is a function of concentration. In the case of Ni(II) the highest detectable molar mass exceeds 350.000 g/mol indicating a high binding affinity of the ligand and Ni(II). Due to the positive charge MEPEs can be assembled in multilayers using the ELSA protocol.

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

Polyoxometalate Clusters (POMs)

The ELSA method was applied to incorporate negatively charged POMs into thin multilayers. The conditions of adsorption and the structure of the layers were characterized in detail. Through experimental conditions during deposition, we can tailor the surface coverage of POMs, as well as their electrochemical properties, and the permeability of the multilayers. The electrochemical properties of the POM-clusters are fully maintained in the ELSA films. We identified the Preyssler-type heteropolytungstate $[\text{Eu}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$ as attractive component in electrochromic devices. The electrochromic display shows excellent stability, suitable response time, low power consumption, and sufficient optical contrast.

We show that encapsulation of POMs with suitable surfactants is an efficient way to modify the surface chemical properties of POM-clusters including solubility, adhesion, and phase behavior. The surfactant encapsulated clusters (SECs) form Langmuir monolayers at the air-water interface, which are readily transferred onto solid supports.

Using catalytically active POM-clusters and dendritic amphiphiles, we prepared and tested the first catalytic SEC systems (dendrzymes) in analogy to naturally occurring enzymes. The discrete core-shell structure was elucidated by neutron scattering and molecular modeling.

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1990: Diplom (MS), Chemistry (Rheinisch-Westfälische Technische Hochschule Aachen, RWTH Aachen)
Thesis: Preparation, Characterization, and Reactivity of Molecular Films on Metal-Oxide Surfaces.

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

1994: Post-Doctoral Fellow (Université Louis Pasteur, Strasbourg)

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

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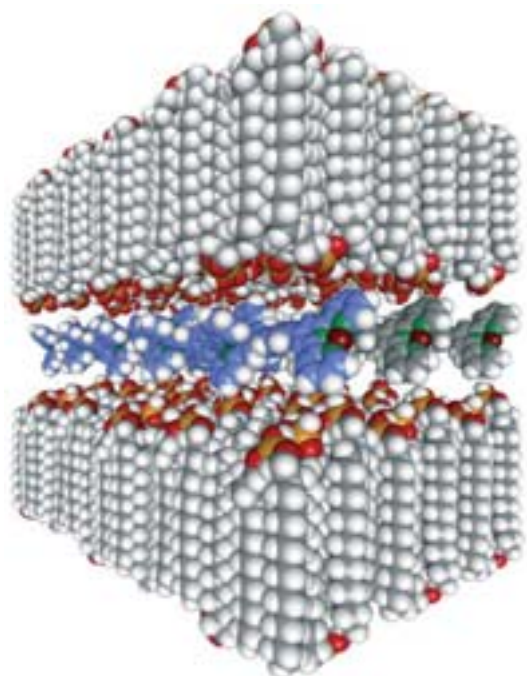


Fig. 1: Representative structure of a PAC mesophase derived by X-ray scattering methods and molecular modeling

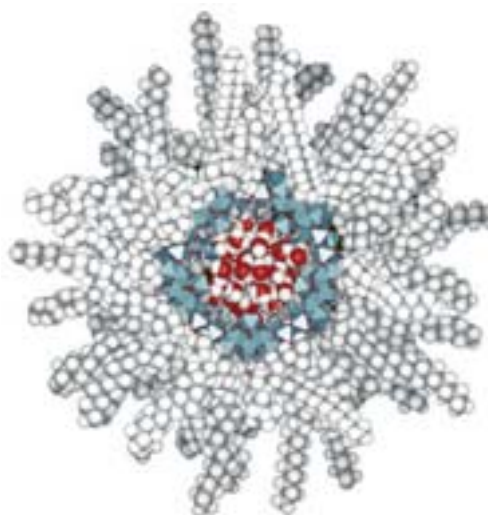


Fig. 2: Molecular modeling study of a surfactant-encapsulated POM cluster. The interior of the Keplerate cluster is filled with water molecules, the exterior is decorated by didodecylammonium molecules.

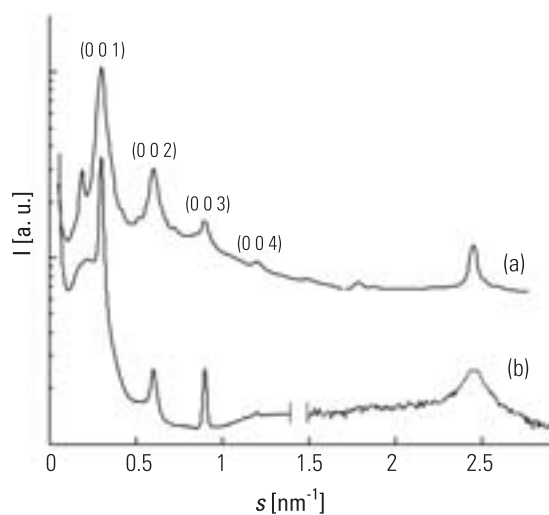


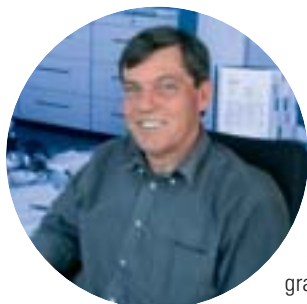
Fig. 3: Calculated (a) and experimental (b) small and wide angle X-ray scattering patterns of PAC. The molecular modeling study shown in Fig. 1 is based on this data.

Key Publications:

- [1] Kurth, D. G., Severin, N. and Rabe, J.: Perfectly Straight Nanostructures of Metallosupramolecular Coordination Polyelectrolyte–Amphiphile Complexes on Graphite. *Angew. Chem.* 41 (2002) 3833, *Angew. Chem. Int. Ed.* 114, 3681(2002).
- [2] Liu, S., Kurth, D. G., Volkmer, D.: The Structure of Layer-by-Layer Self-Assembled Multilayers with Polyoxometalate Nanoclusters. *J. Am. Chem. Soc.* 124, 12279 (2002).
- [3] Liu, S., Kurth, D. G., Möhwald, H. and Volkmer, D.: A Thin Film Electrochromic Device based on a Polyoxometalate Cluster. *Adv. Mater.* 14, 225 (2002).

NON-PLANAR INTERFACES

Bioinspired Control of Electrical and Optical Properties of Interfaces



Aims:

Learning from principles of natural photosynthesis interfaces and films shall be constructed that enable

- efficient energy transfer,
- charge separation,
- electron transfer along a polarity gradient and
- conversion of the electrical energy

into chemical energy.

The experiments are of exploratory nature to elucidate the role of the interface to control the processes.

Results:

· Incorporating chromophores in multilayer films either as planar films or as walls of hollow capsules the energy transfer between these chromophores could be established. This is understood since high enough chromophore concentrations can be easily achieved to obtain interchromophore distances below a "F \ddot{o} rster radius" of 5nm. Also energy donor and acceptor, if coupled to a polyelectrolyte can be arranged along the surface normal to enable energy transfer along this normal.

· Measured via the dependence of pyrene emission spectra on polarity it was shown that polyelectrolyte multilayers of polarity depending on the chemical nature of the polyelectrolytes can be built. By consecutive adsorption of different polyelectrolytes it was therefore also possible to set-up polarity gradients across nm dimensions.

- For efficient electron transfer between chromophores the interchromophore distance should be at least below 3 nm requiring very high chromophore concentrations. Coupling pyrene to a polyelectrolyte with high doping content (1:30) and then building a film with this polymer these high concentrations could be established.
- To enable kinetic studies of the electron transfer (in coop. with University of Potsdam) the films could also be build up as hollow capsules thus yielding sufficient optical density and low light scattering. The observed transients suggest that indeed vectorial photoinduced electron transfer has been achieved.

Future Work:

- Confirm and quantify the measured vectorial electron transfer (coop. University of Potsdam)
- Study processes for molecules more similar to natural systems (porphyrins) or more suitable for electron transfer (cyanine dyes, functionalized fullerenes)
- Study transfer mechanisms near electrodes by Raman spectroscopy (cooperation TU Berlin)

As a new direction we have started to investigate alignment of magnetic particles in magnetic fields and at interfaces (D. Wang). There a crucial parameter is the control of the particle coating either inhibiting aggregation or enabling it in a controlled way. The particles will be embedded in a matrix with switchable solvent content and viscosity.

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1971: Diploma, Physics

(University G \ddot{o} ttingen)

Thesis: Messungen der absoluten Polarisation optischer \ddot{U} berg \ddot{a} nge an Molek \ddot{u} len und Molek \ddot{u} lkomplexen in Fl \ddot{u} ssig-Kristallinen L \ddot{o} sungsmitteln

1974: PhD, Physics

(University G \ddot{o} ttingen, Max-Planck-Institut f \ddot{u} r Biophysikalische Chemie, A. Weller, E. Sackmann)

Thesis: Lokalisierte und delokalisierte Triplettzust \ddot{a} nde in Einkristallen von Elektron-Donor-Akzeptor-Komplexen:

ESR- und emissionspektroskopische Untersuchungen zwischen 4K und 300 K

1974-1975: Postdoc (IBM San Jose)

1975: Research Assistant

(University of Ulm)

1978: Habilitation, Physics

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Thesis: Transporteigenschaften und Phasen \ddot{U} berg \ddot{a} nge in organischen Charge-Transfer Kristallen

1978-1981: Scientific Coworker

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1981: Associate Professor C3, Experimental Physics (TU M \ddot{u} ncchen)

1987: Chair C4, Physical Chemistry, (University of Mainz)

Since 1993: Director and Scientific Member (Max Planck Institute of Colloids and Interfaces, Golm)

Since 1995: Professor, Physics and Physical Chemistry (University Potsdam)

Since 2001: Honorary Professor (Zhejiang University, Hangzhou)

Energy Transfer (ET) on Light-Harvesting Capsule to Mimic Photosynthesis

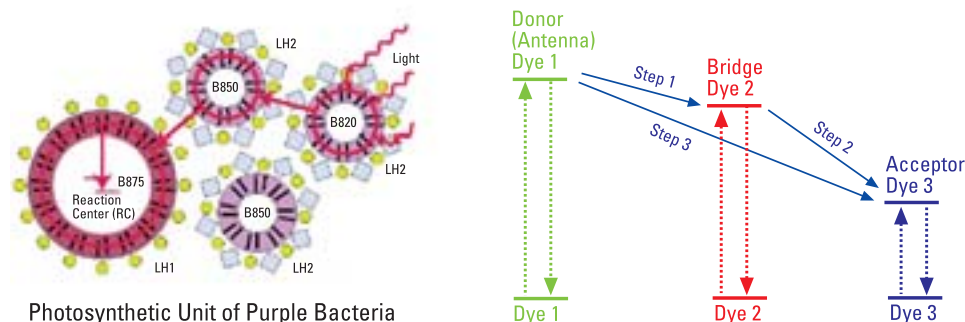


Fig. 1: Scheme of antenna function of the photosynthetic unit (left) and energy level scheme of dyes at dyes used for realization in synthetic systems

Energy Transfer Perpendicular to a Capsule Surface by LbL Assembly of Dyes on Capsules

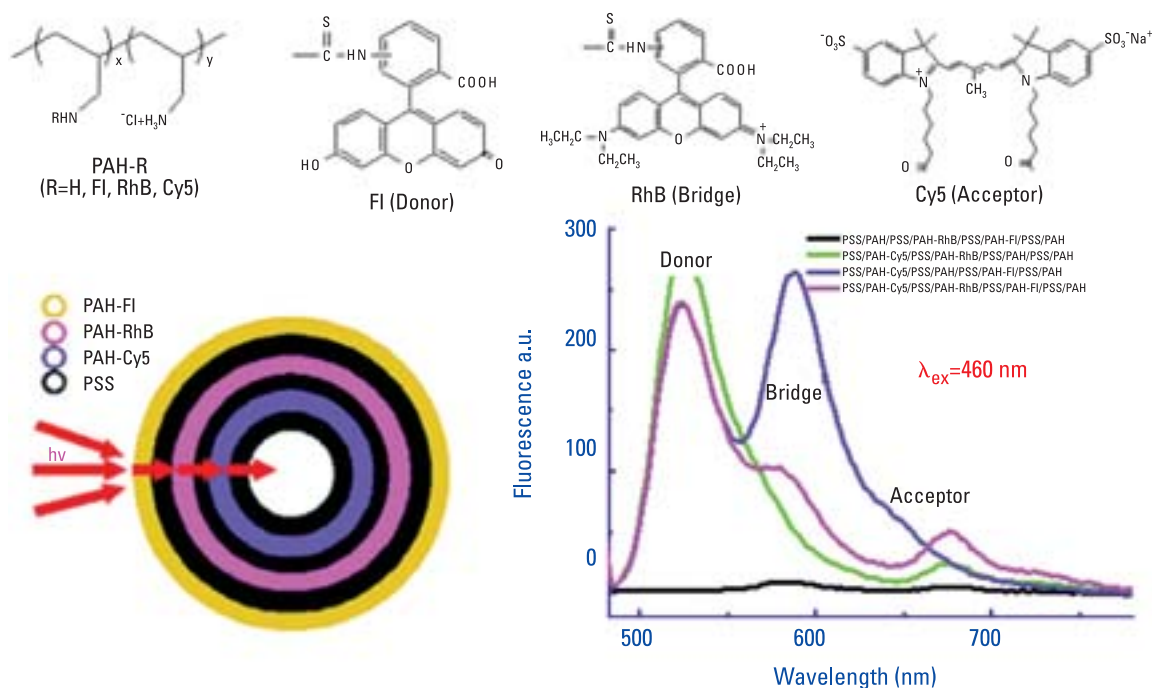


Fig. 2: Energy transfer in chromophore containing capsules schematically (left) and measured via fluorescence emission (right)

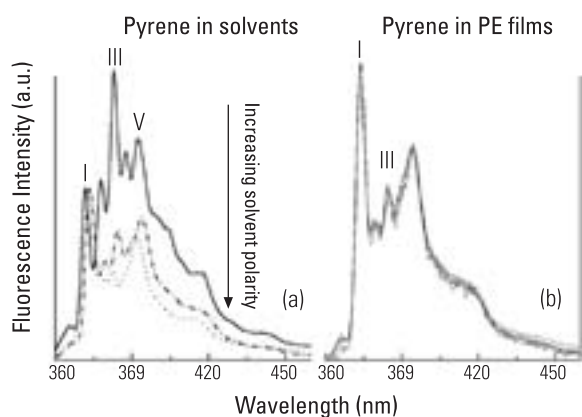


Fig. 3: Fluorescence emission of pyrene in solvents of different polarity (left) and in polyelectrolyte films (right)

Key Publications:

- [1] Tedeschi, C., Caruso, F., Möhwald, H. and Kirstein, S.: Adsorption and Desorption Behavior of an Anionic Pyrene Chromophore in Sequentially Deposited Polyelectrolyte-Dye Thin Films. *J. Am. Chem. Soc.*, 122, 5841-5848 (2000).
- [2] Tedeschi, C., Möhwald, H. and Kirstein, S.: Polarity of Layer-by-Layer Deposited Polyelectrolyte Films As Determined by Pyrene Fluorescence. *J. Amer. Chem. Soc.* 123, 954-960 (2001).
- [3] Dai, Z. F., Dähne, L., Donath, E., Möhwald, H.: Downhill energy transfer via ordered multi-chromophores in light-harvesting capsules. *J. of Phys. Chem. B*, 106, 11501-11508 (2002).

Dynamics of Complex Polymer Layers



Aims:

Organic multilayered materials can be built up by self-assembly at solid interfaces, e.g. by employing electrostatic interactions of polyelectrolytes or other organic components. While structural properties of such complex layers can easily be monitored by standard techniques, it is a far more challenging task to probe dynamic aspects and internal interactions. The latter should, however, play an important role for the stability and macroscopic properties of these materials.

Our research group is dedicated to the establishment of new methods to study dynamics, hydration and local interactions in layered organic materials. As dynamic probes for these properties, either fluorescent dyes, incorporated into the films, or nuclear spins in NMR studies are employed. Planar layer systems are investigated by fluorescence techniques, while layers prepared on the surface of colloidal particles ('Coated Colloids') are the subject of NMR investigations, which are a very recent approach in multilayer studies.

Results:

Lipid Monolayers coupled to Polyelectrolyte Surfaces

Internal interfaces in organic layer systems are studied by determining diffusion coefficients of lipids in a monolayer in contact with polyelectrolyte multilayers. Ultraslow diffusion is investigated by an interference FRAP (fluorescence recovery after photobleaching) setup. Lipid diffusion coefficients and activation energies for diffusion are measures of the binding strength at the internal interface.

Variation of the charges of the lipid head group and the last polyelectrolyte layer, respectively (**Table 1**), provide evidence of the dominance of strong attractive electrostatic interactions, even for the case of successive negative layers. The polyelectrolyte multilayers are flexible to rearrange, such that binding can take place even to loops of the second outermost layer. Thus, surprisingly, activation energies reflect the number of binding lipid charges, but are independent of their sign of charge.

Interactions are furthermore modified by the presence of water or other solvent molecules. In water-swollen layers, diffusion coefficients are increased and are larger for zwitterionic lipids than for ionic head groups. Fluorescence resonant energy transfer experiments prove the effect of water on interlayer-distance.

Thus, by employing FRAP, the interaction strength at internal interfaces in multilayer assemblies can be characterized. Current interest lies in extending these studies to weak interactions, and the role of hydration in uncharged coupled layers.

Polyelectrolyte Multilayers: Reversible Swelling

Multilayers of alternately charged polyelectrolytes are prepared by self-assembly. The hydration of multilayers adsorbed to colloidal particles in a dilute aqueous dispersion is studied via the 1H -NMR relaxation rate R_2 of water protons. A specific relaxation rate R_{2sp} is a measure for water immobilization, reflecting both a) the fraction of bound water molecules and thus the hydration of the layers, and b) the average mobility of the layer bound water molecules and exchangeable polymer protons.

For multilayers of $(\text{PAH/PSS})_n$, an alternating water immobilization is observed with increasing layer number (**Fig. 2**). This is interpreted as an influence of the electric potential of the outer layer on the multilayer system, since the effect is independent of the nature (strong or weak PE) of the outer layer: A positive surface charge leads to a larger fraction of immobilised protons within the multilayers, while a negative surface charge decreases 1H immobilisation. Such a surface-potential driven swelling is attributed to non-compensated charges within the multilayer assembly, which lead to reversible effects of either water uptake or water structuring.

Solvent relaxation is furthermore applied to investigate further internal properties of polyelectrolyte multilayers, such as protonation. pH-dependent water relaxation shows that the internal protonation is governing the magnitude of surface-potential driven water immobilization effects.

Solvent relaxation is furthermore employed to study the affinity of multilayers for solvent mixtures, where it is found that PSS/PDADMAC layers show a higher immobilization of alcohols, and can thus be considered more hydrophobic as compared to PSS/PAH multilayers.

Thermoreversible Polymers at Interfaces

[in collaboration with D. Kuckling and P. B. Welzel (Dresden), and A. Larsson (now: YKI, Stockholm)]

The thermoreversible polymer PNIPAM, which shows a coil to globule transition in solution, is co-polymerised with charged groups in order to combine temperature sensitive properties with electrostatic self-assembly.

In a first step, the phase transition in monolayers on colloidal silica is investigated by 1H NMR to monitor the mobility of the loops and tails, and by DSC measurements. The phase transition is broadened due to motional restrictions. Charges on the chain cause an incomplete transition due to electrostatic repulsion from the surface. **Fig. 3** gives the fraction of liquid spins which do not undergo a transition to the solid phase. The transition thus becomes incomplete even at a charge content which does not affect the transition of coils in solution.

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1996-1998: Postdoc, Physical Chem-

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Since 1998: Group Leader

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The fundamental investigations of the phase transition properties in confined geometry give important hints to achieve temperature-controllable properties in multilayers: A new approach to build multilayers containing thermoreversible components is thus based on the idea of a spatial separation of the electrostatic and the thermoreversible function.

This is achieved by the use of a grafted side chain copolymer with charged side chains and a thermoreversible backbone. Employing such novel building blocks, appropriate preparation conditions were found to form multilayers on colloidal templates as well as on planar substrate.

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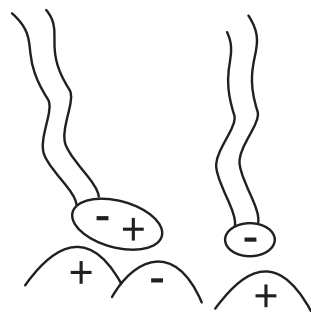


Fig. 1: Model of lipids in monolayers interacting with charged loops of polyelectrolyte multilayers. In air, the zwitterionic lipid shows a stronger interaction than the anionic one.

Key Publications:

[1] Wang, L., Schönhoff, M. and Möhwald, H.: Lipids Coupled to Polyelectrolyte Multilayers: Ultraslow Diffusion and the Dynamics of Electrostatic Interactions. *J. Phys. Chem. B* 106, 9135-9142 (2002).

[2] Schönhoff, M., Larsson, A.; Welzel, P. B. and Kuckling, D.: Thermoreversible Polymers adsorbed to Colloidal Silica: A 1H NMR and DSC Study of the Phase Transition in Confined Geometry. *J. Phys. Chem. B* 106, 7800-7808 (2002).

[3] Schwarz, B. and Schönhoff, M.: Surface Potential driven Swelling of Polyelectrolyte Multilayers. *Langmuir* 18(8), 2964-2966 (2002).

ΔE [kJ]	Outer layer: PSS(-)	Outer layer: PAH(+)
DMPC(+/-)	10.7 ± 0.7	12.1 ± 1.5
DOPC(+/-)	10.6 ± 1.6	
DOPA(-)	8.0 ± 0.9	6.9 ± 0.5

Table 1: Activation energies ΔE of lipid diffusion in monolayers in contact with polyelectrolyte multilayers

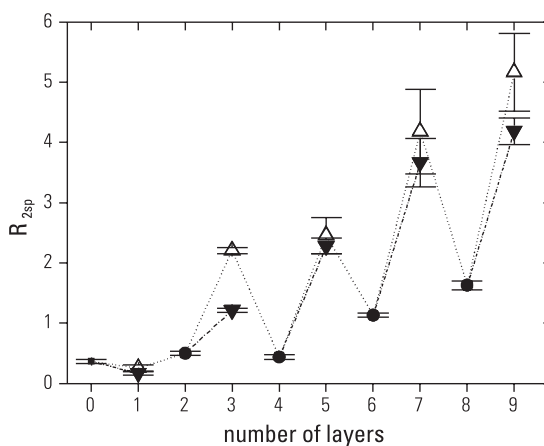


Fig. 2: Specific relaxation rate R_{zsp} for multilayers of $(PAH/PSS)_n$ with different polyelectrolytes as last layers:
 •: PSS (even number of layers), Δ : PAH (odd number of layers), and \blacktriangledown : PDADMAC on top of $(PAH/PSS)_n$

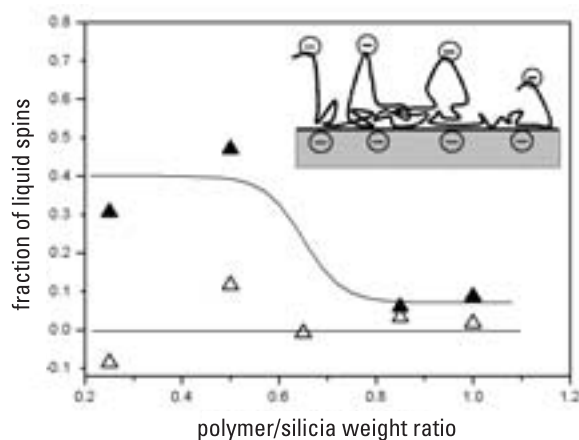


Fig. 3: Fraction of polymer segments in loops and tails, which remain mobile above the phase transition. Δ : PNIPAM (uncharged), \blacktriangle : charged copolymer. Inset: Model of charged segments preventing collapse.

NON-PLANAR INTERFACES

Multifunctional Polymeric Micro- and Nanosized Capsules



Aims:

- Nano-engineered ultrathin shell assembly on colloidal particles (study on permeability and release of small molecules)
- Hollow capsules (core decomposition, polymer segregation in multilayers caused by pH, solvent, temperature in order to broaden the possibilities to control the incorporation of macromolecules in capsules, single molecules effects)

- Stimuli-responsive capsules
- Chemical reactions in restricted volumes (precipitation of small organic molecules in capsules, study of their crystalline structures, synthesis of inorganic particles in the capsules)
- Enzymatic reaction in the capsule and artificial cells.

Results:

Permeability as a Function of Salt:

Permeability coefficients changed from 1.0×10^{-7} to 6.6×10^{-8} m/sec at pH 7.0 and from 4.5×10^{-9} to 8.7×10^{-9} at pH 8.0, while the salt concentration was varied from 500 to 10 mM. Influence of the ionic strength and pH on the permeability of PSS-PAH multilayer capsules for fluorescein molecules revealed the following general ideas:

- The permeability through the multilayers occurs mostly through cavities in the polyelectrolyte complex
- Increase of the ionic strength decreases the free energy of polyelectrolyte interactions which proportionally influences the permeability
- The dissociation of the PSS-PAH bonds with increasing of the pH leads to repulsive forces between the induced negative charge of the PSS segments inside the multilayers and negative charges of the permeating fluorescein molecule, decreasing the permeation rate.

Hollow capsules were fabricated using the layer-by-layer self-assembly process employing completely biocompatible components – polymeric micro-/nano-particulate templates composed of polylactide homo-/co-polymers and polyelectrolytes approved for human application. These structures were characterized for their physicochemical properties and explored for probable applications in drug delivery.

Preparation of Thermosensitive Microcapsules:

Thermosensitive hollow capsules were successfully prepared by electrostatic self-assembly of oppositely charged block copolymers containing a NIPAM block. We showed that the morphology (size, wall thickness) of the capsules changes upon annealing due to the shrinking of the polymer chains in the polyelectrolyte complex. This process yields a strong decrease of the permeability of the shell for small molecules. This feature gives a possibility to tune the release properties of the capsules.

Nano-Engineered Capsules as Stimuli-Sensors and Microreactors:

The capsules have been loaded with polymers by synthesis with a view to introduce stimuli-responsive polymers. First, poly(sodium styrene sulfonate) was synthesized and it can interact with yttrium ions. In the presence of Y^{3+} , the PSS loaded capsules were shrunk and became deformed. This phenomenon was reversible, addition of EDTA furnishing again the initial capsules by relaxation. Work is under progress about other stimuli-responsive polymers bearing acidic or basic functions (pH-responsive), complexant moieties (metallic ion-responsiveness), or gelling polymers (temperature-responsive). Such polymers can also act as adsorbents for substrates or as catalysts, and will thus be used for chemical reactions inside the capsules (microreactors).

Metallized Colloids and Hollow Capsules:

A novel type of silver-filled microcapsules was fabricated by means of electroless deposition of silver onto the surface of a sacrificial core followed by coating with polyelectrolyte multilayer and core decomposition. The resultant capsules contain silver particles of few tens of nanometers in diameter both in the capsule wall and capsule interior. The silver-containing capsules catalyze reduction of 4-nitrophenol into 4-aminophenol by $NaBH_4$. The catalytic activity was found to be higher than that of the native silver sol and the reaction could proceed under alkaline conditions, which is usually not possible.

Two systems are being developed to analyze microcapsule morphological changes under flow and to study their mechanical properties. A parallel-plate flow chamber was built to study the shear stress effect on microcapsules when adsorbed on a modified surface. The observation of the capsules exposed to shear is suggested to extend the understanding of their mechanical behavior and to obtain information about the adhesion strength between differently modified surfaces.

A microfluidic system was designed, fabricated and implemented to study the behavior of capsules flowing in channels with dimensions and geometries simulating blood vessels. A silicon component contains microchannels that lead into 10 μm constrictions, which were fabricated using lithography techniques. Labeled polyelectrolyte microcapsules (average size 20 μm) were introduced into the system. Their behavior at the constrictions was visualized through fluorescence microscopy. The recovered capsules were further analyzed, appearing to have undergone a plastic deformation.

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1991: Diploma, Physics (Lomonosov Moscow State University)

1994: PhD, Biophysics, (Lomonosov Moscow State University)

Thesis: Formation and Investigation of multilayer films containing nucleic acids

1994-1996: Postdoctoral Researcher (Institute of Physical Chemistry, University of Mainz, Germany)

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1997-2000: Postdoctoral Researcher (Max Planck Institute of Colloids and Interfaces, Golm)

2001-2002: Scientist (Capsulation NanoScience AG, Berlin)

Since 2001: Group Leader (Max Planck Institute of Colloids and Interfaces, Golm)

Chemical Reaction in Restricted Volumes:

The Presence of the polyacid in the capsule volume results in pH values shifted to acidic and the total shift could reach up to 4 pH units. Such conditions inside the capsules suffice to force the precipitation of pH sensitive materials exclusively in their interior.

The synthesis of inorganic substances exclusively inside polyelectrolyte capsules was performed. Due to the high pH inside the polycation filled capsules the selective synthesis of magnetic Fe_3O_4 and non-magnetic hematite Fe_2O_3 particles inside the polyelectrolyte capsules filled with polycation was demonstrated. The structure of the resulting particles depends on ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the outer solution. The synthesized Fe_2O_3 and Fe_3O_4 core / polyelectrolyte shell composites were characterized by TEM and WAXS techniques. Besides magnetite different ferrites (CoFe_2O_4 , ZnFe_2O_4 , MnFe_2O_4) were synthesized from corresponding salts exclusively inside polyelectrolyte capsules of 10 μm diameter. Polyelectrolyte capsules with synthesized ferrite (magnetite) particles possess magnetic activity high enough to be easily manipulated in water solution by an external magnetic field. The use of hollow polyelectrolyte capsules as microreactors for spatially restricted inorganic synthesis was shown to be a perspective for further investigation.

Hollow polyelectrolyte capsules covered with lipids have been introduced as a promising alternative to liposomes, because of their higher mechanical stability and uniform size distribution. In order to reduce the ion permeability, different mixtures of phospholipids and cholesterol were applied. The ion permeability was estimated by the osmotic shrinkage of lipid coated capsules in presence of salt. Addition of 30% (w/w) cholesterol to a DPPA/DPPC (1/9) lipid mixture enhanced the osmotic reaction of the capsules significantly.

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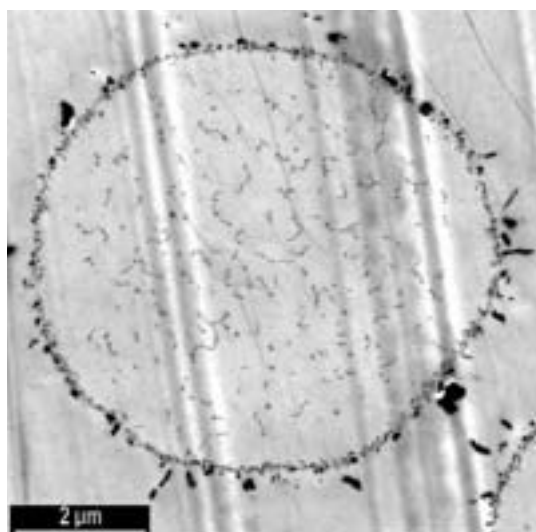


Fig. 1: TEM of thin slice of the silver-filled capsule



Fig. 2: Image demonstrating 20 μm capsules flowing through 10 μm constriction

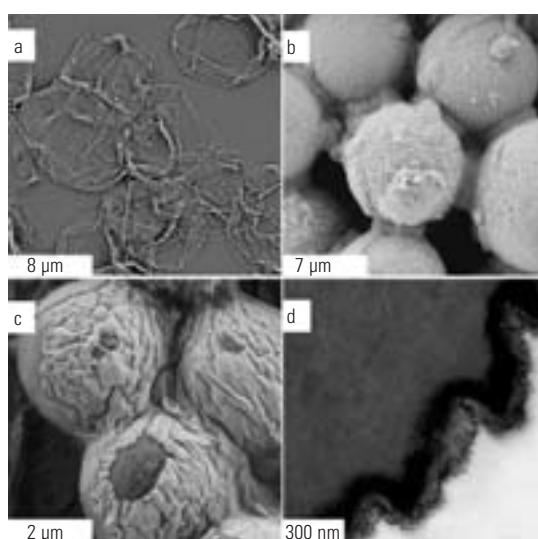


Fig. 3: SEM images of hollow polyelectrolyte capsules (a) and polyelectrolyte capsules filled with Fe_3O_4 (b) and YF_3 (c). (d) – TEM image of an ultramicrotomed polyelectrolyte capsule filled with Fe_3O_4

Key Publications:

- [1] Tiourina O. P, Radtchenko, I., Sukhorukov G. B., Mohwald, H.: Artificial cell based on lipid hollow polyelectrolyte microcapsules: Channel reconstruction and membrane potential measurement. *Journal of Membrane Biology*, 190 (1): 9-16, 2002.
- [2] Antipov, A. A., Sukhorukov, G. B., Fedutik, Y. A., Hartmann, J., Giersig, M., Mohwald, H.: Fabrication of a novel type of metallized colloids and hollow capsules. *Langmuir* 18 (17): 6687-6693, 2002.
- [3] Shchukin, D. G., Radtchenko, I. L., Sukhorukov, G. B.: Synthesis of Nanosized Magnetic Ferrite Particles Inside Hollow Polyelectrolyte Capsules, *J. Phys. Chem. B*, 107, 86-90, (2003).

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



Summary:

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

Aims:

The focus is on the following topics/questions:

- Nucleation: What processes govern two-dimensional nucleation for different surface coverage and cooling rates?
- Interfacial molecular ordering: What is the interfacial molecular ordering as a function of temperature, surface coverage, and preparation history?
- Domain morphologies: Into which domain morphologies aggregate the interfacial molecules under various growth conditions?
- Statics and dynamics of wetting: What is the relation between the interfacial alkane ordering and the statics and dynamics of wetting?
- Viscoelastic properties: What are the viscoelastic properties of molecularly thin organic films?

Results:

The centre box (red frame) of **Fig. 1** shows the various topologies of molecularly thin films of long chain alkanes at SiO_x/air interfaces as a function of the surface coverage and the temperature. The dashed vertical line separates low surface coverage on the right ("submonolayer coverage") from higher surface coverage ("excess coverage") on the left. Increasingly lighter blue represents increasing temperatures. The boxes to the left and the right show examples for experimental observations in various temperature ranges.

Excess Coverage

In the case of excess coverage the amount of alkane is sufficient for more than one complete alkane monolayer (with the molecules oriented upright). For this coverage three temperature regions can be distinguished. Above the surface freezing temperature, T_{sf} , all the alkane is liquid and forms a completely wetting, molten film. Between the surface freezing and the bulk melting temperature (T_{bulk}), liquid alkane partially wets (as droplets) an interfacial solid alkane monolayer. Below T_{bulk} various droplet and solid bulk topologies are observed, depending on the preparation history.

The upper box on the left shows the x-ray diffraction intensity of a sample with slightly more than one monolayer coverage as a function of temperature. The diffraction intensity below T_{bulk} originates from the molecular ordering in the interfacial monolayer. Quite remarkably, the diffraction signal does not vanish above T_{bulk} (T_{bulk} is indicated by the dashed line). There is molecular ordering even above T_{bulk} , i.e. alkanes at solid/gas interfaces show the rare phenomenon of surface freezing (the common behavior of most substances is surface melting). In recent years, we have investigated

extensively excess and submonolayer coverages by x-ray diffraction and x-ray reflectivity. There is now a detailed picture on the various molecular orderings (crystalline and rotator phases) in the vicinity of the bulk and surface freezing temperatures.

The topology and phase behavior below T_{bulk} is quite complicated and depends on the cooling rate and the degree of undercooling. Upon substantial undercooling (>15deg) the droplets solidify straightforward into amorphous bulk. For small undercooling (a few degrees centigrade), nucleation and bulk solidification is very unlikely in spite of the contact of the liquid bulk droplet with the solid monolayer. In this case, typically the majority of the liquid droplets remain completely unchanged for many hours, only very few solidify spontaneously into amorphous (polycrystalline) bulk. A significant fraction of the droplets shows a peculiar behavior. Disks of ordered (solid), planar alkane multilayers grow radially out of the liquid droplets (see lower box on the left of **Fig. 1**). The concentric multilayer disks coexist with the liquid bulk droplets in their center. The decreasing droplet sizes indicate that they serve as alkane source for the radially growing multilayer disks. On rare occasions the growth of the alkane multilayers starts only on one side of the liquid droplet. This creates an interfacial energy gradient which leads to a lateral droplet movement. The droplet "advances" while leaving behind a trail of solid alkane multilayer. If the temperature is raised to above T_{bulk} , the droplet movement first stops and then it "recedes" on its own trajectory while "eating up" (melting) the solid multilayer trace which it had been creating at lower temperatures. In rare cases, liquid droplets on multilayer plateaus attain a "star-shape". A preliminary explanation assumes that the liquid droplet is covered with a single solid alkane mono/multilayer domain which causes the sixfold anisotropy of the surface tension.

Submonolayer Coverage

In the case of submonolayer coverage the amount of alkane is not sufficient for a complete monolayer. Above a temperature very close to T_{sf} of the excess coverage, an all-liquid alkane melt completely wets the substrate. Below T_{sf} , the alkanes aggregate into domains with the molecules oriented normal to the interface (i.e. all alkane is solid below T_{sf} and there is no " T_{bulk} "). The nucleation, growth and morphology of these domains depend on the cooling rate, the surface coverage and the preparation conditions/history. "Solution growth" (solvent evaporation at T below T_{sf}) typically leads to dendritic domains (see upper box on the right of **Fig. 1**). If the liquid alkane film is cooled below T_{sf} ("melt growth") the domains have typically a fractal seaweed-like shape (lower box on the right). The relation between cooling rate and number of domains can be explained to a first approximation by the classical nucleation theory. The relation between surface coverage and nucleation rate is not yet understood. An analysis of the morphological patterns is currently under way. Three different growth regimes have been identified. It is assumed that they reflect fundamental differences in the alkane supply of the solidification front ("depletion", "balanced", and "excess" growth).

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Since 1994: Group Leader

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1996: Habilitation (Mainz University)

Thesis: Grenzflächeninduzierte Strukturbildung in monomolekular dicken organischen Schichten bei der Langmuir-Benetzung und auf planaren Festkörperoberflächen

Recently, also the viscoelastic properties of alkane layers were studied. **Fig. 2** shows an example of "force spectroscopy" of a solid alkane monolayer. The force distance curve is obtained by punching a hole through the layer with a surface microscopy tip. One can see how upon approaching the layer the microscope tip senses the layer surface first as weakly attractive, then as stronger repulsive force. Upon pressing with more than 200 nN (≈ 2 GPa) the tip finally breaks through the layer and reaches the substrate surface. Upon retreating, the tip again remains stuck at the layer surface until sufficient force leads to the final "snap-off". The local slope of the curve reflects the viscous layer properties. The viscoelastic properties change significantly with temperature and can be related to the interfacial alkane ordering (phases).

Future Perspectives:

From our studies we expect general new insights into two-dimensional nucleation and domain growth phenomena. For instance, we hope to learn more about the conditions for two-dimensional nucleation, e.g. how the nucleation-activation barrier depends on the surface coverage and which role the shape (length) of the molecules plays. From the analysis of the domain morphology we expect new insights into the impact of the local molecular transport on the domain structure and the molecular ordering (e.g. two- vs. three-dimensional transport, melt vs. solution, etc.). From the wetting studies we want to reveal details on the relation between

the wetting topology (wetting kinetics) and the interfacial molecular ordering. These wetting studies will also disclose details on the lateral molecular transport on top of the multi-layers growing radially from the central liquid bulk droplet (the growth source). This topic is further directly connected to the viscoelastic behavior of alkane mono- and multilayers and surface friction which will be addressed by force spectroscopy.

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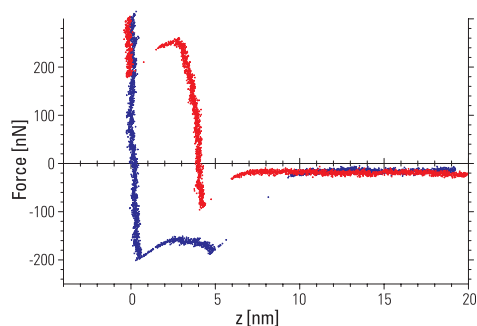


Fig. 2: Force spectroscopy of a solid alkane monolayer on a SiO_2 -surface. The red curve is obtained on approach, the blue one on receding of the tip to/from the surface.

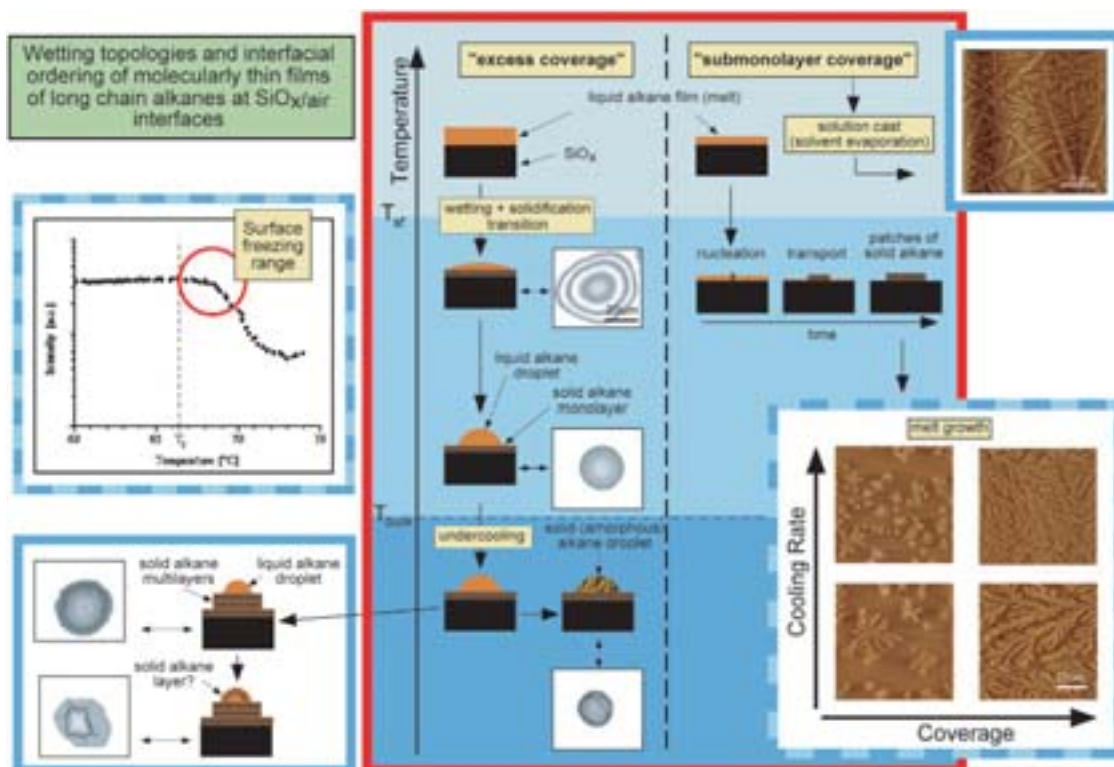


Fig. 1: Overview over the various interfacial ordering, nucleation and wetting phenomena of long chain alkanes at solid/air interfaces

Key Publications:

- [1] Schollmeyer, H., Ocko, B. and Riegler, H.: Surface Freezing of Triacotane at SiO_2 /Air Interfaces: Submonolayer Coverage. *Langmuir* 18, 4351-4355 (2002).
- [2] Riegler, H. and Essler, F.: Polyelectrolytes. 2: Intrinsic or Extrinsic Charge Compensation? Quantitative Charge Analysis on PAH/PSS Multilayers. *Langmuir* 18, 6694-6698 (2002).
- [3] Schollmeyer, H., Struth, B. and Riegler, H.: Long chain n-alkanes at SiO_2 /air-interfaces: Molecular ordering, annealing, and surface freezing of triacotane in the case of excess and submonolayer coverage. *Langmuir*, in press.

Assembly of Complex and Biomimetic Materials



Complex Molecular Assembly in Aqueous Solution

Aims: Molecular assembly of multi-components provides the possibility of wide structural and functional characterization as potential intelligent materials.

Results: Surfactant and polyelectrolyte are well known to form ordered three-dimensional, stoichiometric, highly stable complexes in aqueous solution. Such structure formation is based on the polymers charged backbone, electrostatic and hydrophobic interactions. By using such complexes as templates one may fabricate nanostructured semiconductor materials (CdS) with lamellar morphology in a long range order.

Enzymatic Reaction via Molecular Recognition

Aims: An enzymatic hydrolysis reaction accompanying molecular recognition can help to understand the recovery of membranes in living systems.

Results: Optical microscopy is used to follow the enzyme influence on molecular arrangement, catalytic activity and impact of inhibitor. It has been verified that the selected inhibitor has inhibited the cleavage of the L-DPPC monolayer by PLA₂. The enzymatic hydrolysis reaction has been dynamically observed with Brewster angle microscopy. Addition of an indole derivative as inhibitor postponed the formation of "C" or "O" types of domains, and correspondingly delayed the cleavage of L-DPPC. Our experimental results provide a possibility for a direct proof of an inhibitor capacity.

Mixed Lipid/Protein Complexes at Interfaces

The complex film of the lipids, L- α -dipalmitoyl-phosphatidic acid (DPPA), L- α -distearoyl-phosphatidylcholine (DSPC) and the protein human serum albumin (HSA) has been investigated by grazing incidence X-ray diffraction (GIXD). The measurements provide a direct evidence for the interactions and binding of HSA to phospholipid monolayers. The GIXD data obtained for the coupled layers show that HSA changed the diffraction pattern and phase sequence of the anionic DPPA dramatically by binding and electrostatic screening, while no change of the phase behavior was found for the zwitterionic DSPC monolayers.

Biointerfacing Microcapsules

Aims: For controlled and sustained release it is important to reduce the permeability of capsules for small polar species, which in most cases enable small molecules to diffuse easily through the polyelectrolyte capsule walls. In order to imitate the barrier function of biological membranes, it was thus attempted to assemble lipids on the PE capsules to reduce the permeability for ions and small neutral molecules. The lipid may form bilayer structures and in some cases also multilayers on the capsule surface. This then provides the possibility to incorporate membrane specific components like channels and receptors for specific permeation and recognition.

Results: Mixtures of the phospholipids, L- α -dimyristoyl-phosphatidic acid (DMPA), and L- α -dipalmitoyl-phosphatidylcholine (DPPC), have been successfully adsorbed onto the charged surface of multilayer polyelectrolyte capsules to form a novel vesicle.

Leaving such vesicles in phospholipase A₂ solution we observed the hydrolysis reaction on the surface of the lipid/polymer vesicles and permeability change before and after reaction by confocal laser scanning microscopy (CLSM). Thus a capsule with permeability adjustable by enzymatic hydrolysis of the lipid layers adsorbed on the surface of a multilayer polyelectrolyte capsule was constructed.

Biogenic Capsules

Polyelectrolyte capsules were made by coating size controlled templates with alternating polyelectrolyte adsorption and followed by removal of the templated cores. However, if core dimensions approach the persistence length and charge density for sufficient coating, this is especially demanding for biocompatible materials. Therefore, as an important extension of shell materials the preparation of biogenic capsules with properties as good as hitherto for synthetic polymers is the next challenge. Proteins and their mixture with lipids as efficient encapsulation materials can meet perfectly the demand.

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1989: Diploma, Chemistry

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Thesis: Photon Correlation Spectroscopy Investigation of Ultrafine Polymer Particles

1992: PhD, Chemistry

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Thesis: Homodyne Correlation Spectroscopy of Macromolecular Ultrafine Particle in Solution and Dynamic Light Scattering of Thermally Excited Capillary Waves on a Liquid Surface

1993: Postdoc (Foundation for Research and Technology – Hellas)

1993-1996: Postdoc

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1996-1999: Full Professor

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Since 1999: Full Professor

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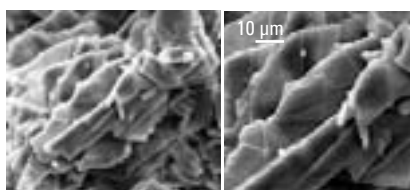


Fig. 1: SEM images of the lamellar CdS crystals

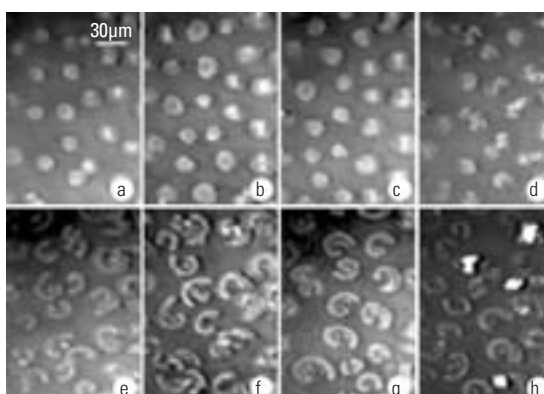


Fig. 2: BAM images of a mixed monolayer of inhibitor/L-DPPC (30:1) after injection of PLA₂. The images were taken 0 (a), 6 (b), 55 (c), 60 (d), 67 (e), 74 (f), 77 (g), 78 (h) minutes after starting the hydrolysis reaction at $\pi_0 = 12 \text{ mNm}^{-1}$.

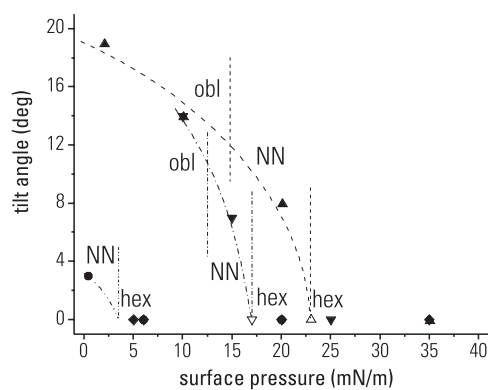


Fig. 3: Phase diagram (tilt angle t as a function of lateral pressure π) of DPPA monolayers on pure water (▲), on buffer (▼), on HSA (essentially fatty acid free) solution (●) and on HSA (glycated) solution (◆). Open symbols represent extrapolated values. obl (oblique with intermediate tilt), NN (rectangular with NN tilt) and hex (hexagonal, non-tilted).

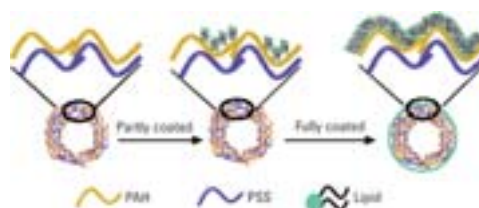


Fig. 4: Scheme for the surface of polyelectrolyte capsules, partly lipid covered capsules and fully lipid covered capsules.

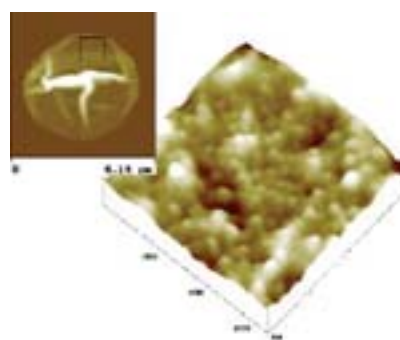


Fig. 5: SFM image of multilayer polyelectrolyte capsules fully covered by pure DMPA in a dried state and a selected dried (PSS/PAH)₂/DMPA surface morphology.

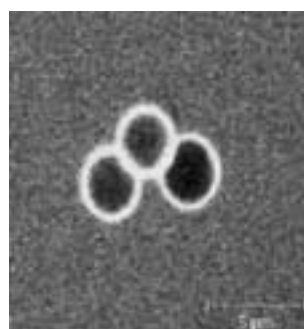


Fig. 6: CLSM image of a partly PLA₂ catalyzed capsule. The dye molecules can penetrate into the capsule, but the dye concentration inside is lower than outside.

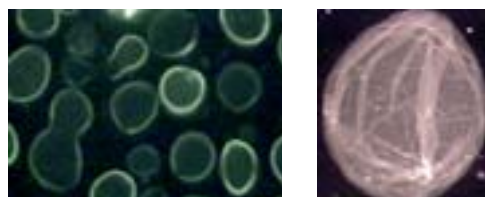


Fig. 7: Fluorescence microscopy images of protein capsules in aqueous solution and in a dried state.

Key Publications:

- [1] Li, J. B., Zhang, Y., Yan, L. L.: Multilayer formation on a curved drop surface, *Angew. Chem. Int. Ed.* 40, 891-893 (2001).
 [2] Zhang, H. J., Cui, G. C., Li, J. B., Morphological investigation of mixed protein/phospholipids monolayers, *Colloids & Surfaces A*, 201, 1-6 (2002).
 [3] He, Q., Li, J. B.: Dynamic and morphological investigation of phospholipid monolayer hydrolysis by phospholipase C. *Biochem. Biophys. Res. Comm.* 300, 541-545 (2003).

Research Group Nanotechnology for Life Science

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



The new research group Nanotechnology for Life Science started on April 1st 2002. It is founded to evaluate the possibilities of collaborations between the Max Planck Society (basic research) and the Fraunhofer Society (applied research). The partnership of both institutions is a joint group between the Fraunhofer IAP and the MPI of Colloids and Interfaces. It is the first time that both institutions

have worked together on such a pilot project.

For a period of six years, young researchers from both institutions have been developing polymeric nanosystems as biomimetic materials and membrane-like structures as well as nanometer sized particles [1, 2, 3]. The nanosystems act either as defined interfaces between drugs and tissues (drug carrier, drug targeting) or they influence the structures of tissues and the proteins themselves. An illustration of such nanoparticles [8] that could be used as a drug carrier system is shown in Fig. 1.

The new group works closely with the market for drug carriers and drug targeting systems by taking the insights produced by the basic research of the MPI of Colloids and Interfaces and developing them further in the collaboration between MPI of Colloids and Interfaces, Fraunhofer IAP and Industry. The patent for immobilization of retinoic acid by cationic polyelectrolytes, for example, was financed together with the help of the pharmaceutical industry [4].

The long-term aim is the interdisciplinary evaluation of the innovation potential of nanostructured drug carriers. Golm is an ideal site for the work of the group due to the geographic and personal closeness of the MPI of Colloids and Interfaces, the Fraunhofer IAP and the University of Potsdam.

The starting basis for this technical development is a class of biomimetic hybrid systems consisting of polymers, lipids, amphiphiles and surfactants.

In the medium term the work will concentrate on the following areas of research:

- Polymers, proteins und protein stability
- Polymer-lipid nanoparticles as drug carrier systems
- Polymeric gene vectors (non-viral)

The combining element of these subjects is the bottom-up technique for the preparation of tailor-made nanostructures based on the use of polymers and surfactants, which has been reported on in two review articles [5, 6].

Polymers, Proteins and Protein Stability

Amyloid-based diseases of the brain that are either infectious (BSE) or noninfectious (Alzheimer) influence human beings as well as mammals. Such neurodegenerative and lethal diseases are caused by the folding of proteins from α -helix-rich (natural) to β -sheet-rich structures (misfolded). Misfolded proteins grow into plaques which are lethal for the affected person or animal. At present there are no therapies and they are not expected to be developed in the medium term.

Therefore it is the aim of the research group to transform amyloid β -sheet structures into α -helix structures. A new approach using polymeric nanostructures will be applied. The proof of this principle has already been shown in a common work [7]. In conclusion it seems highly probable to control the secondary structure of proteins with polymeric nanostructures. It is a realistic hope that we will be able to develop a tool for the refolding of misfolded proteins and even find a way to avoid amyloid plaque or dissolve the plaque itself.

The cooperation between the MPI of Colloids and Interfaces and the Fraunhofer IAP is a suitable basis to achieve this aim. The previous patent development [7], for example, would not have been possible without the combination of the know-how in polymer synthesis produced by the Fraunhofer IAP and the structure analysis capabilities of the MPI of Colloids and Interfaces.

The cooperation was established, based on this preliminary work, to clarify the molecular mechanisms during the polymer-protein interactions (MPI of Colloids and Interfaces) parallel to the synthesis of optimized polymeric nanostructures, which act as an agent for protein folding (Fraunhofer IAP).

The necessary nanostructures are prepared from polyelectrolytes (including polyamino acids and synthetic DNA) and fluorinated lipids. Their influence on the three steps of the amyloid plaque cascade (misfolding, nucleation and aggregation) is under investigation. Expected results will form a scientific basis for developments in therapeutics for the control of infectious and non infectious amyloid diseases.

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1991: Diploma, Chemistry

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Thesis: Cyclization of Polyacrylonitrile

1995: PhD, Chemistry

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Thesis: Strukturumwandlungen

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Homopolymeren, Copolymeren und

Metallcarbonylen des Acrylnitrils

2000: Postdoc, Research Scientist

(Heinrich-Heine-Universität Düsseldorf)

1995-2001: Group Leader

(Max Planck Institute of Colloids

and Interfaces, Golm)

2001: Habilitation, Physical Chemistry

(Potsdam University)

Thesis: Self-Assembly, Ordered

Nanostructures and Functionality of

Polyelectrolyte-Amphiphile Complexes

Since 2002: Group Leader

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Polymer-Lipid Nanoparticles as Drug Carrier Systems

Complexes formed by polyelectrolytes and oppositely charged lipids are systems which can self-assemble. They form nanostructures that resemble natural membranes such as double-layer membranes formed by phospholipids and cholesterol, which are used for the development of liposomes. The functionality of membranes depends on the proteins on their surfaces which influence the contact with their surroundings. Transmembrane proteins are known, for example, which stabilize the membrane mechanically by coupling with proteins in the cytosol. This principle of mechanical stabilization is used to form the drug carrier systems displayed in **Fig. 1**.

In the case of polyelectrolyte-lipid complexes, the linkage of double-layer forming lipids is performed by complexing the stabilizing polyelectrolyte to each lipid molecule. The complexation itself is reversible. It can be controlled by varying the parameters of the surroundings such as temperature, salt concentration and pH value.

The first aim is to develop a modular drug carrier system, which is tailor made for a specific drug. Polyelectrolyte-lipid complexes with a great variety of possible variations are suitable for this. Pharmaceutically acceptable or biodegradable substances will be used. A large number of properties can be modified by varying the lipid and the polymer. The second aim is to functionalize the nanoparticles of the drug carrier systems to drug targeting systems. This will be done, for example, by protein fragments chemically bound to the surface of the particles. Such functionalized particles bind specifically to organs or regions of the body where the drug is released.

The usability of polyelectrolyte-lipid complexes for the incorporation of lipophilic drugs and for the formation of colloidal dispersions in aqueous media has been shown in basic studies (cf. e.g. **[8]**). Different polymers and lipids were complexed and the resulting structures characterized. A number of drugs were examined for incorporation, the maximum loading was determined and changes of the properties of the carrier systems detected. The local surroundings of the incorporated molecules were investigated using pyrene as a fluorescence probe and model compound. Preliminary techniques were developed based on these investigations to prepare polyelectrolyte-lipid complexes as nanoparticulate dispersions. The stability of the complexes and the release of incorporated molecules were determined as a function of the pH value as well as the salt concentration of the surrounding aqueous medium. Also the surface properties of the particles were modified. A number of physical-chemical properties were implemented by choosing suitable compounds.

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Key Publications:

- [1]** General, S., Rudloff, J. Thünemann, A. F.: Hollow Nanoparticles via stepwise Complexation and selective Decomplexation of Poly(ethylene imine). *Chem. Comm.* 534-535 (2002).
- [2]** Thünemann, A. F., Wendler, U., Jaeger, W., Schnabegger, H.: Nanoparticles of Polyampholyte-Surfactant Complexes with Perfluorododecanoic Acid. *Langmuir* 18, 4500-4504 (2002).
- [3]** Thünemann, A. F., Sander, K., Jaeger, W., Dimova R.: Polyampholyte-Dressed Micelles of Fluorinated and Non-Fluorinated Dodecanoic Acid. *Langmuir* 18, 5099-5105 (2002).
- [4]** Thünemann, A. F.: Immobilization of vitamin A acid by cationic polyelectrolytes. European Patent No. 1003559 and US Patent No. 6,395,284
- [5]** Thünemann, A. F.: Polyelectrolyte-Surfactant Complexes (Synthesis, Structure and Materials Aspects). *Prog. Polym. Sci.* 27, 1473-1572 (2002).
- [6]** Thünemann, A. F., Müller, M., Dautzenberg, H., Joanny, J.-F., Löwen, H.: Polyelectrolyte Complexes in *Advances in Polymer Science, Special Volume: Polyelectrolytes with Defined Molecular Architecture*, Springer: Berlin (in press)
- [7]** Thünemann, A. F., Vieira, E. P., Hermel, H., Motschmann, H., Möhwald, H., Schmah, W., Matiassek, K., Sperling, C., Werner C., In: *Biokompatible Kolloide mit geringer Zelladhäsion und aktiver Stabilisierung von Blutproteinen* PCT/EP01/14542
- [8]** Thünemann, A. F., General, S.: Pharmacological preparation made from a nanoparticulate meso-morphous polyelectrolyte lipid complex and at least one active ingredient. WO 03/000404 A1

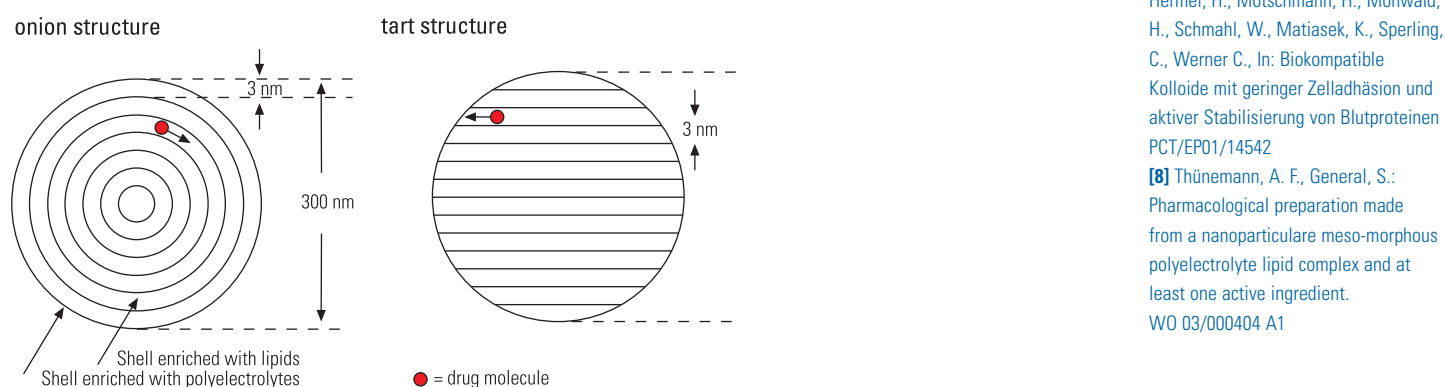


Fig. 1: A schematic representation of a drug carrier system consisting of polyelectrolyte-lipid complexes with a typical size of 300 nm. The stability of the nanoparticles is achieved by the polymers. The inner structure of the particle with a characteristic length of 3 nm is given by the lipids. A lipophilic drug molecule is displayed in red, which can diffuse only within the lipophilic regions (displayed in white). Regions displayed in black (formed by the polyelectrolytes) form a diffusion barrier for the drug (cf. patent application of Fraunhofer IAP and MPI of Colloids and Interfaces **[8]**).