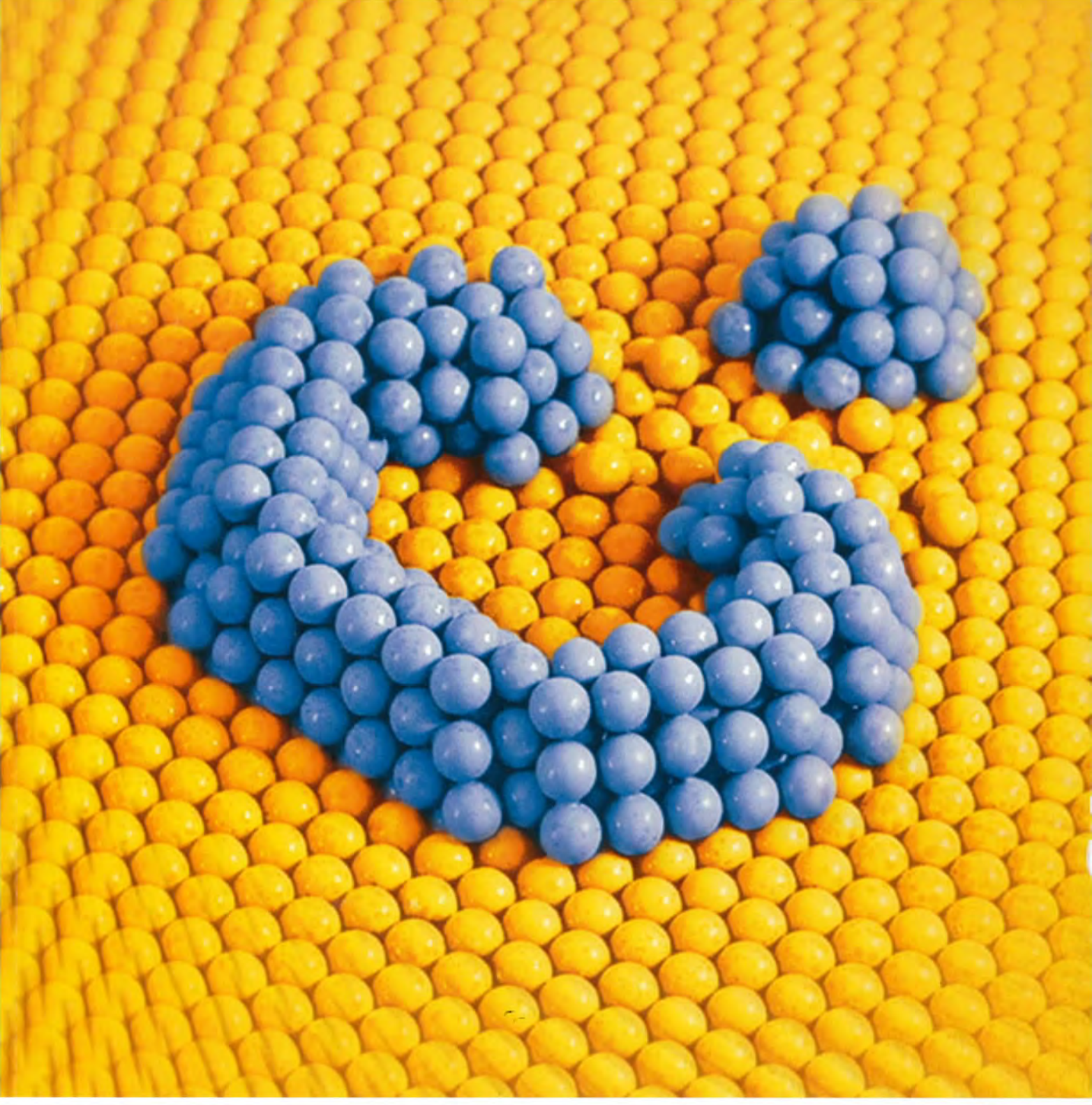

Max Planck Institute of Colloids and Interfaces

BIANNUAL REPORT 2003-2004

MAX-PLANCK-GESELLSCHAFT

Max Planck Institute of Colloids and Interfaces

BIANNUAL REPORT
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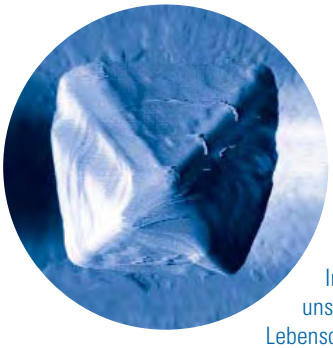


Kolloide sind Teilchen oder Tropfen im Größenbereich zwischen einigen Nanometern und Mikrometern. Die Kolloid- und Grenzflächenforschung ist daher „Nanowissenschaft". Allerdings war dieses Schlagwort noch nicht in Mode, als das Institut 1992 gegründet wurde. Aber auch in diesem Fall hätte das Institut nicht diesen Namen angenommen, da unsere Forschung langfristig angelegt ist und die Lebensdauer von vorübergehenden Strömungen überschreiten sollte.

Kolloide sind allgegenwärtig im täglichen Leben und der Natur, so z.B. in Farben, Tinten, Getränken, Lebensmitteln oder pharmazeutischen Rezepturen. Blut, Zellen oder Knochen sind Beispiele für kolloidale Systeme. Infolgedessen ist der Umgang mit ihnen beinahe so alt wie die Menschheit, und auch ihre Erforschung ist älter als 100 Jahre. Warum war es also vor 13 Jahren dann an der Zeit, unser Institut mit Konzentration auf die Grundlagenforschung aufzubauen?

Aufregende Entwicklungen in den letzten zwei Jahrzehnten haben dazu beigetragen, die Beschäftigung mit kolloidalen Systemen von einer Kunst in eine Wissenschaft zu verwandeln. Seitens der Herstellung gab es erhebliche Fortschritte innerhalb der supramolekularen Chemie, die es ermöglichten, das Wechselspiel verschiedener schwacher Wechselwirkungen zu kontrollieren. So konnten größere funktionelle Einheiten aufgebaut werden, deren Struktur von der Umgebung abhängt (Responsive Systeme). Die Herstellung organischer und anorganischer Nanopartikel konnte über Nichtgleichgewichtsbedingungen und Grenzflächen kontrolliert werden. Das ermöglichte wiederum deren zielgerichtete Selbstorganisation in hierarchische Verbundsysteme und/oder meso- und nanoporöse Strukturen. Entwicklungen der Charakterisierungsmethoden wurden sehr wichtig für das Verständnis von Struktur und Funktion der Systeme. Dies ist eine große Herausforderung im Größenbereich zwischen nm und µm, wo die Ordnung, wenn überhaupt vorhanden, nur gering ist. Beispiele für diese Methoden sind Techniken, um fluide Grenzflächen spezifisch zu studieren wie Röntgen-, Neutronen- und Lichtstreuung, nichtlineare optische Spektroskopie und FTIR-Spektroskopie sowie optische Mikroskopien. Einzelne Partikel werden durch analytische Ultrazentrifugation, Einzelteilchenlichtstreuung, optische und Ramanmikroskopie sowie Kraftspektroskopie mit kolloidalen Sonden charakterisiert. Kolloidale Assemblagen werden dagegen beschrieben, indem die Möglichkeiten von optischer und Elektronenmikroskopie sowie Synchrotron-Röntgen-Streutechniken ausgebaut werden, um an mikrometergroßen Teilen einer Probe zu streuen. Die permanent zunehmende Leistungsfähigkeit von Computern ermöglicht das Studium von Systemen, die erheblich oberhalb von molekularen Dimensionen liegen. Dazu wurden auch neue Algorithmen und neue analytische Theorien entwickelt. In den verschiedenen Beiträgen dieses Berichts werden Sie sehen, dass das Institut eine führende Rolle bei diesen Entwicklungen gespielt hat, so auch in den letzten beiden Jahren.

Da Kolloide und Grenzflächen überall zu finden sind, ist ihr Verständnis sehr wichtig. Existierende Systeme und Prozesse können so verbessert und neue entwickelt werden, so dass sie technisch und ökonomisch einsetzbar werden. Die Forschung am Institut ist daher anwendungsnah, und, um nicht den Fokus auf die innovativste strategische Forschung zu verlieren, entwickelte man verschiedene Kooperationsprojekte mit mehr anwendungsorientierten Partnern (Industrie, Fraunhofer-Institute, pharmazeutische und medizinische Institute sowie Kliniken). Wir empfinden die Unterstützung der Anwendungen als Verpflichtung gegenüber der Gesellschaft, aber sie ist auch eine Quelle der Inspiration für neue Probleme und Aufgaben.

Die Kolloid- und Grenzflächenforschung ist nur durch Längenskalen definiert, jedoch nicht durch irgendeine Materialklasse organischen, anorganischen oder biologischen Ursprungs. Größere Durchbrüche sind zu erwarten bei Kombination der Vorzüge verschiedener Materialien. Unsere Forschung ist daher in hohem Maße interdisziplinär. Sie finden Beiträge aus allen größeren Teilgebieten der Chemie, aus Biochemie und Biophysik, Polymerchemie und -physik und allgemeiner experimenteller und theoretischer Physik sowie Beiträge, die den Übergang in verschiedene Bereiche von Materialforschung, Medizin und Pharmazie markieren.

Viele Institute, auch andere MPI, arbeiten mittlerweile auf diesem Gebiet, und es bietet tatsächlich genügend aufregende Probleme für Kooperation und Koexistenz. Damit stellt sich die Frage nach dem „Alleinstellungsmerkmal" unseres Instituts. Sein Schwerpunkt liegt zwischen Physik und Chemie. Ein Großteil der Arbeiten wird jedoch durch die Natur inspiriert, auch die Forschung mit synthetischen Materialien. Wir versuchen zudem, zum Verständnis der Natur oder zur Lösung medizinischer Probleme beizutragen, z. B. bei Wirkstoffapplikationen oder der Diagnose von Knochenerkrankungen. Daher beschlossen wir vor mehr als sechs Jahren, ehe das Schlüsselwort in Mode kam, als gemeinsamen Schwerpunkt die „Biomimetik" zu entwickeln. Deshalb wurde auch die Einrichtung der vierten Abteilung „Biomaterialien", deren vollständige Funktion Sie diesem Bericht entnehmen können, zu einem zentralen Baustein, um unser Profil zu schärfen. Dieses wurde von der Öffentlichkeit sowie den Förderinstitutionen wahrgenommen. Das Forschungs- und Lehrprogramm zu diesem Gebiet, die International Max Planck Research School „on Biomimetic Systems" und das „Marie Curie Early Stage Training Netzwerk on Biomimetic Systems", beide koordiniert von R. Lipowsky, reflektieren den Erfolg.

Was Sie nicht in harten Zahlen finden werden:

- Das Institut ist zu einer Größe von 280 Personen gewachsen. Weiteres Wachstum ist durch den Raum begrenzt.

- Die zunehmenden Einschränkungen für MPI bezüglich Antragstellung bei DFG und BMBF verringern erheblich unsere Möglichkeiten, nationale Drittmittel einzuwerben. Das konnte glücklicherweise durch EU-Projekte mehr als ausgeglichen werden.

- Die Ausbildung von Wissenschaftlern auf allen Stufen der Karriere war sehr erfolgreich. Jährlich werden etwa 25 Doktorarbeiten fertig gestellt und zwei Wissenschaftler auf permanente Professurenstellen im In- oder Ausland berufen.

- Da die Zahl deutscher Doktoranden bundesweit ansteigt, gilt das auch für den Anteil der deutschen Doktoranden am Institut (Gesamtzahl 70). Die Zahl ausländischer Doktoranden nimmt dagegen ab, auch da die Universität Potsdam die Beteiligung von Doktoranden als Lehrende fordert. Dennoch bleibt der Anteil der Ausländer am Institut mit etwa 40 % stabil, da moderne Forschungsthemen und Laboratorien sowie der Großraum Berlin das Institut für Gäste attraktiv machen. Das schlägt sich auch im letzten „Ranking" der Humboldt-Stiftung nieder. Bezogen auf den Etat belegt das Institut den Spitzenplatz bei Langzeitgästen, die von der Stiftung gefördert wurden.

Letzteres beweist, dass das Institut internationale Anerkennung errungen hat, und auch der Dialog mit der Öffentlichkeit entwickelt sich erfolgreich. So konnten wir unser 11-jähriges Jubiläum im November 2003 mit dem Ministerpräsidenten des Landes Brandenburg Matthias Platzeck, der Ministerin für Wissenschaft, Forschung und Kultur des Landes Brandenburg Johanna Wanka, dem Hauptredner und Präsidenten der Gesellschaft Deutscher Chemiker Fred R. Heiker sowie mit vielen Kollegen und Kooperationspartnern der umliegenden Universitäten und Forschungsinstitute feiern. Unter unseren Kooperationen wurde die zur Humboldt-Universität zu Berlin besonders verstärkt. Das manifestiert ein Kooperationsvertrag sowie die Berufung von Jürgen Rabe von der HU Berlin als Auswärtiges Wissenschaftliches Mitglied an unser Institut.

Dieser Bericht ist das Werk vieler: Von denen, die Beiträge als Gruppenleiter oder Direktoren geschrieben haben und denen, die wie Katja Schulze als PR-Referentin die Beiträge und die Zusammenstellung koordiniert haben. Zuallererst profitiert der Bericht jedoch von den wissenschaftlichen, technischen und administrativen Mitarbeitern, die dafür sorgen, dass wir von Ergebnissen berichten können, die Sie als Leser hoffentlich aufregend finden.

Als scheidender Geschäftsführender Direktor danke ich allen Mitarbeitern für ihre vielen, oft nicht erwarteten Beiträge und wünsche viel Freude und Anregungen beim Lesen.

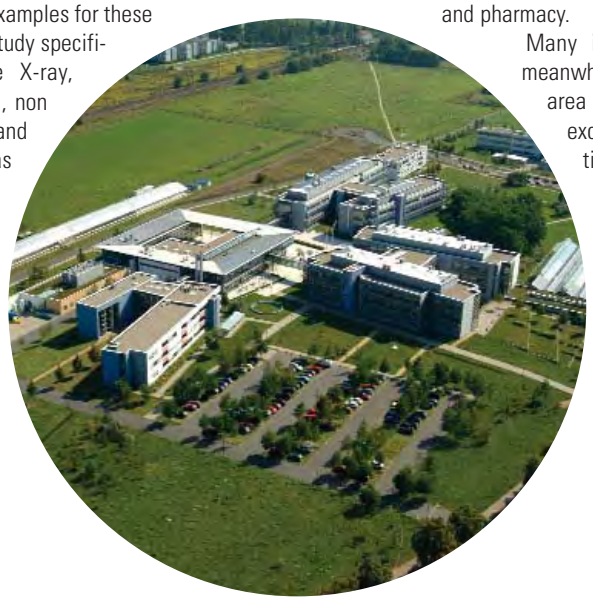
Helmuth Möhwald
Geschäftsführender Direktor 2003-2004

Preface

Colloids are particles or droplets in the size range between some nano- and micrometer, which relates colloid and interface research to nanoscience. This word was not as fashionable as today when the institute was founded in 1992. Even now we would not take up this name since the long-term perspective of the research at the institute should last longer than any fashion.

Colloids are ubiquitous in daily life and in nature, e.g. in paints, inks, drinks, food, pharmaceutical formulations, and blood, cells or bones are colloidal systems. Consequently handling of these systems is almost as old as mankind and also research on them is more than 100 years old. Why then has it been timely to set up our institute about 13 years ago with a mission in basic science?

There have been exciting developments in the last two decades that helped converting art into science when dealing with these systems. On the preparative side there has been much progress in supramolecular chemistry enabling one to control the interplay of different weak interactions to construct larger functional units with structures depending on environmental conditions, i.e. (responsive systems). Preparation of organic and inorganic nanoparticles could be controlled via non-equilibrium conditions and interfaces. This again enabled their directed self-assembly into hierarchical composites and/or meso- and nanoporous structures. Developments of characterization techniques have been extremely important to enable understanding of structure and function of these systems, which is very demanding for the size range between nm and µm where often the order if existing at all, is not very pronounced. Examples for these methods are techniques to study specifically fluid interfaces like X-ray, Neutron and light scattering, non linear optical techniques and FTIR-spectroscopy as well as optical microscopies. Individual particles can be characterized with high sensitivity by analytical ultracentrifugation, single particle light scattering, optical and Raman microscopy and colloidal probe force spectroscopy.



Colloidal assemblies can be characterized by extending the possibilities of optical and electron microscopies and developing synchrotron X-ray techniques to be able to scatter from micron-sized spots. The ever increasing computer power has enabled studies of systems well above the molecular size. For this also new algorithms have been developed as well as new analytical theories. You will find in various contributions in this report that the institute has played a major role in these developments also in the last 2 years.

Since colloids and interfaces are present everywhere their understanding is obviously most helpful to improve existing systems and processes and to develop new ones to become technically and economically feasible. Thus research in the institute is close to applications, and in order not to loose focus on most innovative strategic research we have developed various ways of collaborative projects with more application oriented partners. These are in industry, in Fraunhofer institutes as well as in pharmaceutical and medical institutes and clinics. Supporting applications we feel an obligation towards society, but it is also source of inspiration for new problems and tasks.

Colloids and interfaces research is only defined by length scales, but not by any class of materials of organic, inorganic or biological origin. Major breakthroughs are expected combining the virtues of different materials, and therefore our research is highly multidisciplinary. You will find contributions from all major chemical disciplines, biophysics and biochemistry, polymer physics and chemistry and general experimental and theoretical physics and also the outreach towards various areas of materials science, medicine and pharmacy.

Many institutes, also other MPI, meanwhile perform research in the area and, indeed, it offers enough exciting problems for cooperation and coexistence of these institutes. This, however, raises the question on the uniqueness of our institute. It is centred between physics and chemistry but much of our research also with synthetic materials is inspired by nature. We also intend to contribute to an

understanding of nature or to solving medical problems, e.g. in drug delivery or diagnosis of bone diseases. Hence, more than 6 years ago, before this key word became fashionable we decided as common focus "Biomimetics". Accordingly the establishment of the 4th department "Biomaterials" which you will find in full function in this report has become a central asset to sharpen our profile. It has also been recognized by the public as well as funding agencies, and the research and teaching programme on this subject, the International Max-Planck Research School and the Marie Curie Early Stage Training Site, both coordinated by R. Lipowsky, reflect the success.

What you will not find in hard numbers in the report:

- The institute has grown to a size of 280 people, and further growth is limited by available space.

- Due to inner German rules there are growing restrictions on MPI to apply for funding to the DFG and the Federal Ministry for Research and Technology (BMBF). This reduces considerably our national funding resources. It could fortunately be more than counterbalanced by EU projects.

- Education of scientists has been successful at all levels of their career. Annually about 25 thesis are completed, and we had on average 2 calls per year on tenured professor positions in Germany or abroad.

- Since the number of German graduate students is increasing nationwide the fraction of German graduate students (altogether 70) is again increasing. The number of foreign graduate students is decreasing, also since the University Potsdam now requests graduate students to be involved in teaching. Still the fraction of foreigners remains at about 40 %, since the modern research topics and laboratories and the location in the greater Berlin area make it attractive for them. This is also reflected in the latest ranking of the Humboldt foundation where, normalized to the budget, our institute was top in terms of long terms guests funded by them.

The latter shows that the institute has acquired an international reputation, and also our local dialogue with the public appears successful. Hence we could celebrate in November 2003 our 11th anniversary with the Minister-President of Brandenburg Matthias Platzeck and with the Minister for Science, Research and Culture of Brandenburg, Johanna Wanka, with Fred R. Heiker President of the German Chemical Society, as main speaker as well as with many colleagues from the universities and research institutions around with whom we collaborate. Among those collaborations that with Humboldt University has been especially strengthened through a collaboration contract and through appointing Jürgen Rabe from Humboldt University as Foreign Scientific Member.

This report is the work of many people: Those who have written contributions, as group leaders and directors. Those who coordinated it like Katja Schulze being responsible for PR. Above all it profits from the scientific, technical and administrative co-workers who took care that we are able to report results which hopefully the reader will find exciting.

As outgoing managing director I thank all co-workers for their many often not expected, contributions and wish you much pleasure and stimulation in reading.

Helmuth Möhwald
Managing Director 2003-2004

Das Forschungsprogramm des Max-Planck-Instituts für Kolloid- und Grenzflächenforschung (MPIKG)

Die Kolloid- und Grenzflächenforschung befasst sich mit Strukturen, die zwischen den Größenbereichen „Nano" und „Mikro" liegen und aufgrund dessen in der Lage sind, die Lücke zwischen Molekülen und Materialien bzw. Bauteilen zu schließen. Zum einen ermöglicht das Verständnis der strukturellen und dynamischen Hierarchien, kolloidale Strukturen zu größeren Einheiten zu verknüpfen; zum anderen ist die biomimetische Forschung in der Lage die strukturellen Lösungen der Natur auf die Entwicklung neuer Materialien anzuwenden. **Fig. 1** stellt diese beiden Grund legenden Aspekte unserer Forschung dar.

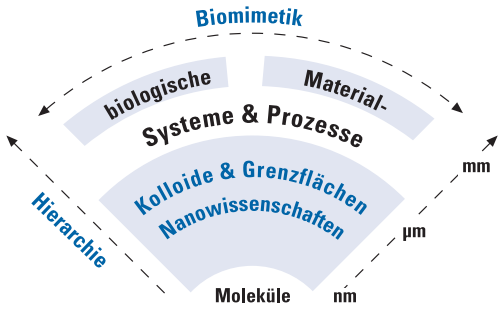


Fig. 1: Die Forschung am MPIKG beschäftigt sich mit Strukturen und Prozessen, die zwischen dem Nano- und Mikrometerbereich liegen und traditionellerweise die Lücke zwischen den hierarchischen Ebenen von Molekülen und Materialien sowie Organismen schließen. Die Erforschung biomimetischer Systeme komplettiert den wissenschaftlichen Zugang, indem es natürliche und künstliche Systeme zueinander in Beziehung setzt.

Das MPI für Kolloid- und Grenzflächenforschung vereint in seinen vier Abteilungen die Bereiche Chemie, theoretische und experimentelle Physik, physikalische Chemie und Materialwissenschaften und besitzt so ein breit gefächertes Fundament an Wissen.

Die Funktionsweise biologischer Systeme und technischer Materialien hängt größtenteils von der Struktur und Dynamik auf der submikroskopischen Ebene ab. So können 20 Aminosäuren und vier Nukleotide biologische Polymere, Proteine und DNA mit nanometergroßen Strukturen ausbilden. Das sind Systeme aus Filamenten, Membranen, Ribosomen und verschiedenen organischen Geweben, die sogar Mineralien enthalten können. Sie bilden die Grundlage der extrazellulären Matrix und der Zellen selbst und sind ursächlich für jeden lebenden Organismus. Der Schritt vom biologischen Polymer zur lebenden Zelle läuft im Nanometer- und Mikrometerbereich ab und ist entscheidend für die Funktionalität eines Organismus. Mechanische, optische oder magnetische Materialeigenschaften hängen in hohem Maße von den Strukturen ab, die auf der Nano- bis Mikrometerskala erzeugt werden.

Kolloide und Grenzflächen

Die aktuelle Forschung am Institut konzentriert sich auf die Synthese, den Aufbau und die Analyse von natürlichen und künstlichen Mehrkomponenten-Systemen. Diese sind multifunktional ausgerichtet. Der fachübergreifende Ansatz, der Physik, Chemie, Materialwissenschaften und Biowissenschaften umfasst, setzt sich aus folgenden Aktivitäten zusammen: Studium von Struktur- bzw. Funktionsbeziehungen in hierarchischen biologischen Materialien; Synthese und Aufbau von experimentellen Modellsystemen; Experimentelle Systemcharakterisierung; Entwicklung und Analyse von theoretischen Modellen; Identifizierung von Grund legenden Mechanismen und generellen Prinzipien, die das kooperative Verhalten der Systeme bestimmen.

Die Interaktion von Experiment und Theorie ist notwendig, um ein tieferes Verständnis kolloidaler Ordnung zu erlangen. Diese Erkenntnisse werden für die Verbesserung des Systemdesigns, die Leistungsoptimierung und die Erhöhung der Zuverlässigkeit eingesetzt. Auf diese Weise wird unsere Forschung nicht nur die künftige Technologie, sondern im Zuge des besseren Verständnisses biologischer Systeme auch die biomedizinischen Wissenschaften maßgeblich beeinflussen, so z.B. durch kolloidale Wirkstoff-Transportsysteme oder Veränderungen des Knochenmaterials aufgrund von Krankheit oder medizinischer Behandlung.

Die Synthese von funktionalen kristallinen oxidischen Nanopartikeln und neuen Kohlenstoffformen ist eine Spezialität des Instituts. Diese wird realisiert mit Hilfe von nichtwässrigen Sol-Gelrouten sowie hydrothermalen und bei hohen Temperaturen durchgeführten Karbonisierungen. Die dabei entstehenden Partikel bilden die Basis für neue Sensoren oder funktionale Beschichtungen und können direkt bei der Chromatographie, der Katalyse oder als aktive Füllstoffe in hybriden Materialien eingesetzt werden.

Für die Polymersynthese in Nanopartikeln werden neue Techniken der Heterophasen-Polymerisation erforscht. Umweltfreundliche werden hier mit neuen synthetischen Möglichkeiten verknüpft, so z.B. für die Verkapselung von nanometergroßen Strukturen, die Hybridisierung oder die Grenzflächen gesteuerte Synthese.

Für Wissenschaft und Anwendung ist neben weichen und harten Strukturen die kontrollierte Generierung von nanoskopischen Porengrößen für die Erzeugung von Bulk-Materialien und Filmen bedeutsam. Für die Bildung geeigneter Architekturen und Porengrößen in kristallinen Materialien werden daher Prozessvorlagen entwickelt. Solche Systeme werden voraussichtlich Elektroden, sensorische Beschichtungen, photovoltaische Zellen und elektrochrome Schichten in naher Zukunft verbessern.

Die Forschung an Grenzflächen ist einerseits dadurch motiviert, dass zahlreiche Interaktionen und Eigenschaften kolloidaler Systeme durch die hohe spezifische Oberfläche bestimmt werden. Andererseits ist das Verhalten von Materie nahe Grenzflächen an sich wissenschaftlich bedeutsam und relevant. Zentrales Thema ist die Dynamik des Austauschs von Materie zwischen Grenzfläche, Masse und begleitenden Veränderungen. Dies ist entscheidend für Makromoleküle, die Struktur von Wasser und Hydrathüllen nahe Oberflächen, die Erkennung und Enzymkatalyse sowie die Kristallisation an Oberflächen. Synthetische Methoden wurden für die Manipulation von Partikeloberflächen entwickelt, die ihre Oberflächenaktivität und Biofunktionalität verändern. Des Weiteren wurden sie als Bausteine für supramolekulare Strukturen und Mikro- und Nanocontainer benutzt.

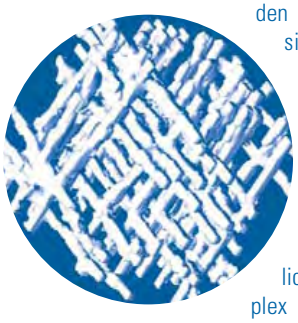
Hierarchische Strukturen

Generell gibt es zwei verschiedene Wege, mit denen man kolloidale Strukturen erzeugen und die Lücke zwischen Molekülen und Materialien oder Bauteilen schließen kann: Bottom-up und Top-down Zugänge. Die Bottom-up Methode beinhaltet Polymerisation, Selbstorganisation sowie Partikelbildung und -wachstum, die Top-down Methode hingegen Dispersion, Druck, Lithographie und Modellbildung. Beide Zugänge finden am Institut ihre Anwendung. So werden viele Methoden der Polymersynthese auf die Bildung komplexer Materialien angewandt. Diese können einerseits vollständig organisch sein wie z.B. Blockkopolymere, wobei ein Baustein hydrophob, der andere hydrophyl ist. Auf diese Weise werden Bilagen und Vesikel ausgebildet. Andererseits können Polymere auch benutzt werden, um die Morphologie wachsender Partikel und Mineralien so zu verändern, dass organisch-anorganische Hybride entstehen. Aus schwachen Interaktionen, die typisch für die supramolekulare Chemie sind, wird besonderer Nutzen gezogen. Die Abhängigkeit der Wechselwirkungen von den umgebenden Parametern befähigt die Systeme, reaktionsfähig und reparabel zu sein.

Die Eigenschaften von Membranen werden theoretisch und experimentell untersucht. Das erfordert eine spezielle technische Ausstattung, da diese in einem flüssigen Medium sich in verschiedenen Aggregatzuständen spontan selbst organisieren. Grenzflächen können in ihrer Funktionsweise optimiert werden, wenn man sie mit weiteren Molekülen und Partikeln bestückt. Eine sehr effektive Methode, um solche Strukturen zu entwickeln, wurde am MPIKG entwickelt und basiert auf der späteren Ablagerung von negativ und positiv geladenen Polyelektrolyten.

Am Institut wird ein großes Spektrum an experimentellen Methoden genutzt, um Struktur und Dynamik von Kolloiden und Grenzflächen zu charakterisieren. Darüber hinaus werden verschiedene Methoden der chemischen Analyse verwendet. Eine entscheidende Herausforderung bildet die simultane Bestimmung von mikro- und nanometergroßen Strukturen in hierarchischen Materialien. Spezielle, kombinierte Zugänge, die auf Scanning Probe Methoden basieren und Elektronen, Photonen und mechanische Spitzen benutzen, wurden ebenfalls am MPIKG entwickelt. Detaillierte Informationen erhalten Sie in den einzelnen Berichten der experimentellen Gruppen.

Biomimetische Systeme



Biomimetische Forschung erstreckt sich von den lebenden Systemen zu den Materialien und umgekehrt (**siehe Fig. 1**): aus der Analyse der Struktur- und Funktionsbeziehungen in den Zellen und der extra-zellulären Matrix ergeben sich vom physiko-chemischen Standpunkt aus notwendige Informationen für den Aufbau von biomimetischen Systemen. Künstliche biomimetische Systeme werden entwickelt, um z.B. technische Probleme mit Hilfe von Strategien für neue Materialien oder technische Geräte zu beheben. Aber sie können auch als Modellsysteme das Verständnis für die natürlichen Vorbilder verbessern, da diese meist zu komplex sind, um mit physikalischen Experimenten oder theoretischen Methoden untersucht zu werden. Dies führt zu einem direkten Einfluss auf die Biomedizin (neue Wirkstoffträger und Behandlungsstrategien) und besseren Methoden für neue biomimetische Systeme.

Derzeit gibt es verschiedene Strategien, um biomimetische Systeme zu bilden. Erstens imitiert man die Bauprinzipien der Natur, vereinfacht jedoch ihre chemische Zusammensetzung. Dabei bilden sich Homopolymere, die nur aus einem Monomer oder aus einem Einkomponentenbilayer und einem Lipid bestehen. Zweitens begrenzt man sich auf bestimmte biologische Subsysteme, die nur eine kleine Anzahl von Komponenten enthalten. Und drittens bildet man hybride Systeme, die eine Kombination von natürlichen und synthetischen Bestandteilen enthalten.

Biologische Systeme bestehen aus einer Hierarchie von Komponenten und Baugerüsten. Auf der kolloidalen Ebene treffen verschiedene Kompartimente aufeinander, die durch geschlossene Membranen und unterschiedliche Gerüste gebildet und durch vernetzte Filamente aufgebaut werden. Hauptfunktion der Membrankompartimente ist, den Raum in einzelne Bereiche zu teilen und den selektiven Transport zwischen den Kompartimenten zu ermöglichen. Die primäre Aufgabe der Filamentgerüste ist die Umstrukturierung der Kompartimente und die Neuorganisation der räumlichen Anordnung.

Die Forschung am MPIKG beinhaltet auch das Studium von natürlichen Materialien (Pflanzenzellwände, Bindegewebe, Knochen) sowie derer Eigenschaften und Fähigkeit zu heilen und sich an wechselnde Umgebungsbedingungen anzupassen. Die Arbeit an biomimetischen Systemen schließt den Aufbau und das Studium verschiedener Kompartimente mit ein: Tröpfchen in Mikro- und Miniemulsionen, an lipide oder polymere Bilagen gebundene Vesikel, an Polyelektrolyt-Multilagen gebundene Kapseln.

In diesen Kompartimenten kann man physikalische und chemische Prozesse der Strukturbildung und Selbst-Organisation durchführen. Sowohl der Top-down als auch der Bottom-up Zugang werden für die theoretische Beschreibung von biologischen und biomimetischen Systemen benutzt. Ersterer basiert auf der Thermodynamik von Grenzflächen und Membranen. Letzterer beginnt bei grob strukturierten Monomer-Modellen und deren Interaktionen, die von einer Vielzahl von theoretischen Methoden, wie sie von der statistischen Physik bereitgestellt werden, untersucht werden.

Ein langfristiges Ziel ist es, multifunktionale Biomaterialien zu verstehen, die auf der Tatsache basieren, dass biomimetische Systeme (z.B. synthetische Polymere) mit biologischen Systemen interagieren können (z.B. Bindung an einen Zellrezeptor). Für die räumliche Anordnung von Zellen in Gewebe werden dabei synthetische Gerüste benutzt. Nützlich wäre es, diese verschiedenen Ebenen in neue multifunktionale Biomaterialien zu integrieren, die hierarchisch aufgebaut sind und mit denen man die verschiedenen strukturellen Ebenen biologischer Systeme separat oder simultan adressieren kann.

Ein weiteres sich abzeichnendes Thema sind aktive biomimetische Systeme: Die Vielseitigkeit von biologischen Systemen ist eng mit der Tatsache verbunden, dass sie aktiv sind, sich neu organisieren können und so die räumliche Struktur auf der Nano- und Mikrometerskala ausbilden. Diese Fähigkeit basiert auf aktiven Nanostrukturen wie z.B. Filament-Monomeren und molekularen Motoren, die exergone chemische Reaktionen katalysieren. Es ist möglich, diese Prozesse mit Hilfe von biomimetischen Modellsystemen nachzubilden und systematisch zu studieren.

Die Aktivitäten über biomimetische Systeme und die Ausbildung von jungen Forschern auf diesem Gebiet werden durch die vom Institut ins Leben gerufene Internationale Max-Planck Research School on „Biomimetic Systems“, die jetzt vom Marie-Curie Early Stage Training Netzwerk komplettiert wird, entscheidend gestärkt und unterstützt. Weitere Informationen über die Graduiertenprogramme finden Sie auf den folgenden Seiten.

Markus Antonietti, Peter Fratzl,
Reinhard Lipowsky, Helmuth Möhwald

The Research Program of the Max Planck Institute of Colloids and Interfaces (MPIKG)

Colloid and interface science focuses on the inter-mediate size range between "nano" and "micro" and bridges the gap between molecules and materials or devices. As shown in **Fig. 1**, two further aspects become important in this type of research. The first is the understanding of structural and dynamical hierarchies in order to link the colloidal size scales to larger entities. The second aspect is biomimetic research which links the structural solutions adopted by nature to those developed for materials.

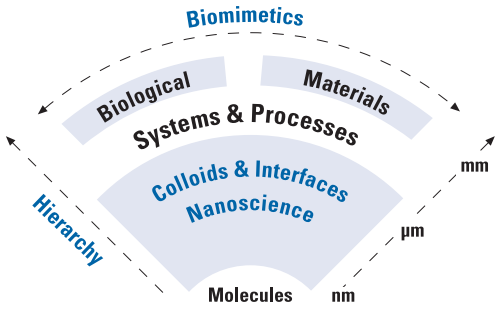


Fig. 1: Research in the MPIKG focuses on structures and processes in the size range between nano and micro, the traditional domain of colloid and interface science, bridging the hierarchical levels from molecules to materials and organisms. Research on biomimetic systems complements this approach by relating natural and artificial systems.

For this type of research, the MPIKG can rely on the expertise in four Departments covering chemistry, theoretical and experimental physics, physical chemistry and engineering.

The way biological systems or technical materials work depends mostly on their structure and dynamics in the submicroscopic range. For example, the relatively small number of 20 amino acids and 4 nucleotides form a multitude of biological polymers, proteins and DNA, with sizes in the nanometer range. They are further assembled into filaments, membranes, ribosomes and various organic tissues which may also contain mineral. These are the building blocks of the extracellular matrix and of the cells themselves, the basis of any living organism. This step from the biological polymers to the living cell covers the range from nanometers to microns and is obviously crucial in defining the functionality of the organism. Very similarly, the functionality of materials, such as mechanical, optical or magnetic properties depend to a large extent on the structures developed in the size range between nano- and micrometers.

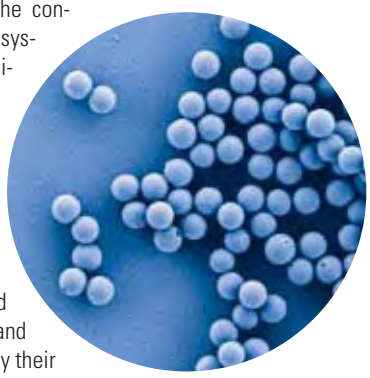
Colloids and Interfaces

Current research at the MPIKG focuses on the synthesis, construction and analysis of multicom-ponent systems, both natural and artificial, which are also multifunctional. This research, which lies at the borderline of physics, chemistry, materials science and bioscience, includes the following activities: Study of structure/function relationships in hierarchical biological materials; Synthesis and construction of experimental model systems; Experimental characterization of these systems; Construction and analysis of theoretical models; Identification of basic mechanisms and general principles which determine the cooperative behavior of these systems.

This interplay between experiment and theory is necessary in order to gain a deeper understanding of colloidal systems. This understanding can then be used in order to improve the design of these systems, to optimize their performance, and to increase their reliability. In this sense, research at the MPIKG will have an impact on tomorrow's technology. Insofar as the understanding of the biological systems themselves is improved, an impact on the biomedical sciences can also be foreseen. Examples include drug-delivery systems based on colloidal systems or changes in bone material quality due to disease or medical treatment.

One synthetic specialty of the institute is the synthesis of functional crystalline oxidic nanoparticles and new types of carbon by non-aqueous solgel routes, hydrothermal and high temperature carbonization pathways. Such particles provide the basis for new sensors or functional coatings, and can be directly applied in chromatography, catalysis, or as active fillers in hybrid materials.

For polymer synthesis in nanoparticles, new techniques of heterophase polymerization are explored. Here, environmental friendliness is combined with new synthetic possibilities, for instance for nanoscale encapsulation, hybridization, or interface driven synthesis.



In addition to soft and hard structures, the controlled generation of nanoscopic pore channel systems into bulk materials and films is of great scientific and application interest. Here, template procedures are developed and applied to design the architecture and the size of pores in crystalline materials in a rational fashion. Such systems will presumably help to make better electrodes, sensing layers, photovoltaic and electrochromic devices in the near future.

Research on interfaces is on the one hand motivated by the fact that many interactions and properties of colloidal systems are determined by their high specific surface. On the other hand the behavior of matter near interfaces in itself is scientifically most important and relevant. Central topics addressed are the dynamics of exchange of matter between interface and bulk and con-

comitant changes, especially for macromolecules, the structure of water and hydration shells near surfaces, recognition and enzyme catalysis and crystallization at surfaces. Synthetic methods have been developed to manipulate the surface of particles which changed their interfacial activity as well as suitability for biofunctionalization and for using them as building blocks for supramolecular structures and micro- and nanocontainers.

Hierarchical Structures

In general, there are two different routes by which one can construct colloidal structures and bridge the gap between molecules and materials or devices: Bottom-up approaches, and top-down approaches. The bottom-up approaches include polymerization, self-assembly, and particle nucleation and growth. The top-down approaches include dispersing, printing, lithography, and prototyping. Both routes are being pursued in the MPIKG. For example, many methods of polymer synthesis are applied to create complex materials. They can be either fully organic, such as block co-polymers, where one block is hydrophobic and the other is hydrophilic, which can form bilayers and vesicles. Polymers can also be used to change the morphology of growing particles and minerals, leading to organic-inorganic hybrids. Special use is made of weak interactions, typical for supramolecular chemistry. Their dependence on environmental parameters enables systems to be responsive and repairable.

The properties of membranes are being studied, both theoretically and by experimentation. This implies special techniques since, when dispersed in a liquid medium, they have the tendency to spontaneously self-assemble into various aggregates. Interfaces can be functionalized by decorating them with additional molecules and particles. A rather powerful method to create such interfacial structures has been developed at the MPIKG, based on the subsequent deposition of negatively and positively charged polyelectrolytes.

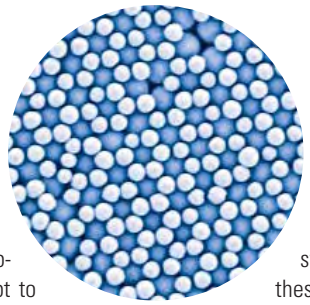
A large spectrum of experimental methods is used at the MPIKG in order to characterize the structure and dynamics of colloids and interfaces. In addition, various methods of chemical analysis are applied. A particular challenge represents the simultaneous determination of structures in the micro- and nano-range in a hierarchical material. Special combination approaches based on scanning probe methods utilizing electrons, photons and mechanical tips are being developed in the MPIKG. More details on the various methods are provided in the reports of the experimental groups.

Biomimetic Systems

Biomimetic research can address both directions of the curved arrow in **Fig. 1**: from the living systems to the material and back. First, the analysis of structure-function relations in cells and extracellular matrix (from a physico-chemical viewpoint) gives the necessary input for building biomimetic systems. Artificial biomimetic systems can then be used to address engineering problems in providing strategies for creating new materials or technical devices. But they can also serve as model systems to improve the understanding of the natural analog, which is usually much too complex to be studied in full detail by physical experiments and, even more, by theoretical modeling. This can have a direct impact in the biomedical field (leading to new drug carriers or treatment strategies, for example) but also lead to improved input for new biomimetic systems.

There are several different strategies by which one can construct biomimetic systems. First, one may imitate the basic construction principle of the biological systems but simplify their chemical composition. This strategy leads to homo-polymers, which consist only of a single type of monomer, or to one-component bilayers, which contain only a single type of lipid. Secondly, one may focus on certain biological subsystems which contain only a relatively small number of components. Thirdly, one may construct hybrid systems which contain a combination of natural and synthetic components.

Biological systems contain a hierarchy of compartments and scaffolds. On the colloidal level of this hierarchy, one encounters various compartments, formed by closed membranes, and different scaffolds, built up from cross-linked filaments. The main function of membrane compartments is to divide space into separate regions and to enable selective transport between compartments. The main function of filament scaffolds is to reshuffle these compartments and to reorganize their spatial arrangement.



Research at the MPIKG involves the study of natural materials, such as plant cell walls, connective tissue and bone, their properties and their capability to heal and adapt to changing environmental conditions. Work on biomimetic systems includes the construction and study of different types of compartments: droplets in micro- and miniemulsions, vesicles bounded by lipid or polymeric bilayers, and capsules bounded by polyelectrolyte multilayers. In all of these compartments, one can perform physical and chemical processes of structure formation and self-organization. Both the top-down and the bottom-up approaches are used for the theoretical description of biological and biomimetic systems. The first is based on the thermodynamics of interfaces and membranes, the second starts from coarse-grained models for the monomers and their interactions, which are studied by a wide range of theoretical methods as provided by statistical physics.

A long-term goal is to conceive multifunctional biomaterials, which are based on the fact that biomimetic systems (e.g., synthetic polymers) can interact with the biological system itself (e.g., bind to a cell receptor). Synthetic scaffolds can also be used for the spatial arrangements of cells into tissues. It would be useful to integrate these different levels into new multifunctional biomaterials which are organized in a hierarchical way and by which one can address, separately or simultaneously, the different structural levels of the biological systems.

Active Biomimetic Systems are another emerging topic: The versatility of biological systems is intimately related to the fact that these systems are active and are able to reorganize and to reconstruct their spatial structure on the nano- and microscale. This ability is based on active nanostructures such as filament monomers and molecular motors which can catalyze exergonic chemical reactions. It is now possible to imitate these processes in biomimetic model systems and to study them in a systematic manner.

In order to support and enhance its activities on biomimetic systems, and to improve the training of young researchers in this emerging field, the MPIKG has created the International Max-Planck Research School on Biomimetic Systems, now complemented by a Marie-Curie Early Stage Training Network, described in detail on the next pages.

Markus Antonietti, Peter Fratzl,
Reinhard Lipowsky, Helmuth Möhwald

Wissenschaftliche Beziehungen

Nationale Kooperationen:
Zwischen dem Max-Planck-Institut für Kolloid- und Grenzflächenforschung und der Universität Potsdam besteht eine intensive und gute Zusammenarbeit, u.a. dokumentiert durch eine Kooperationsvereinbarung aus dem Jahr 1995. Prof. Antonietti, Prof. Lipowsky und Prof. Möhwald sind Honorarprofessoren an der Universität Potsdam mit intensiver Lehrtätigkeit in den Bereichen des Grundstudiums und der Wahlpflichtfächer. Prof. Fratzl ist Honorarprofessor an der Humboldt Universität zu Berlin. Ein Kooperationsvertrag dazu befindet sich in Vorbereitung. Zudem wurde Prof. Rabe (Institut für Physik) 2005 als Auswärtiges Mitglied an das MPIKG berufen.

Ebenfalls in Zusammenarbeit mit der Universität Potsdam wurde darüber hinaus eine „International Max Planck Research School on Biomimetic Systems" erfolgreich beantragt und im Rahmen eines Symposiums im April 2001 eröffnet. Diese hat nach erfolgreicher Evaluierung eine weitere Förderung von 2006-2012 erhalten.

Des Weiteren ist das Institut über den Sonderforschungsbereich (SFB) 448 „Mesoskopische Verbundsysteme" mit der Universität Potsdam und allen Berliner Universitäten verknüpft. Großes Engagement gilt der Betreuung und dem Aufbau von Messplätzen an den Berliner Neutronen- (Hahn-Meitner-Institut) und Synchrotronstrahlungsquellen (BESSY) sowie dem Deutschen Elektronen Synchrotron (DESY) in Hamburg. Insbesondere mit BESSY und der Bundesanstalt für Materialprüfung (BAM) existiert ein Kooperationsvertrag zum Aufbau und zur Inbetriebnahme einer Mikrofokus Beamline.

Internationale Kooperationen:
Im Rahmen von europäischen Förderprogrammen, insbesondere dem 6. Rahmenprogramm der EU partizipieren Arbeitsgruppen des Instituts an Network of Excellence- (NoE), Marie Curie- und Specific Target Research Projects (STREP)- Maßnahmen. Insgesamt laufen zurzeit sechs EU Projekte innerhalb des 6. Rahmenprogramms. Das Marie Curie Netzwerk über „Biomimetic Systems" und das STREP-Netzwerk über „Active Biomimetic Systems" wird vom Institut koordiniert. Weitere Informationen finden Sie unter *www.biomimeticsystems.de* und *www.biomics.de*.

Bilaterale- und Kooperationsprojekte unter der Förderung der European Space Agency (ESA), des Deutschen Akademischen Austausch Dienstes (DAAD), der German Israel Foundation (GIF) for Scientific Research and Development, der VW- und Zeit-Stiftung etc. bestehen zur Zeit mit Frankreich, Bulgarien, Italien, Israel, Dänemark und der Schweiz. Darüber hinaus wird mit dem Ludwig-Boltzmann Institut für Osteologie in Wien an klinisch orientierter Knochenforschung gearbeitet.

Zudam koordiniert das Institut eine Deutsch-Französische Forschergruppe, an der neben den Abteilungen des MPIKG fünf deutsche sowie acht französische Gruppen beteiligt sind. Das Vorhaben wird von DFG, CEA und CNRS gefördert. Informationen finden Sie unter *www.mpikg.mpg.de/crg.*

Nicht zuletzt unterhält die Abteilung Grenzflächen zusammen mit der Chinesischen Akademie der Wissenschaften eine Internationale Partnergruppe in Peking und ein gemeinsames Labor mit dem National Institute for Materials Science (NIMS) in Tsukuba (Japan).

Sehr erfolgreich liefen auch in 2004 die aus dem strategischen Innovationsfonds der MPG geförderten Projekte „Plant Cell Wall" und „ENERCHEM" an.

Industriekooperationen, Verwertungsverträge, Ausgründungen:
Industriekooperationen bestehen u.a. mit der Clariant GmbH, Degussa AG und der Schering AG. Das Institut hält gegenwärtig 20 Patente. Im Zeitraum von 1993-2000 erfolgten insgesamt sechs Ausgründungen: Capsulution Nanoscience AG, Colloid GmbH, Nanocraft GmbH, Optrel, Riegler & Kirstein und Sinterface.

Zusammen mit dem benachbarten Fraunhofer-Institut für Angewandte Polymerforschung erfolgt derzeit der Aufbau einer Nachwuchsgruppe „Polymere Nanotechnologie für die Life Sciences".

Editorial Boards:
Unsere Wissenschaftler fungieren als Gutachter und Berater von fachspezifischen Zeitschriften und Journalen. In der folgenden Liste sind nur die Wissenschaftler angeführt, die entweder Herausgeber oder Mitglied eines Editorial Boards sind.

- *M. Antonietti:* Chem.Mater.; Coll.Polym.Sci.; Langmuir; Macromolecular Journals of VCh; Nach.Chem.Lab.Tech.; New J.Chem.; New Rheol. J.; Prog.Polym.Sci.; Rev.Mol.Biotech.; Small; Soft Matter
- *P. Fratzl:* J. Struct. Biol.; Calcif. Tissue Int.
- *R. Lipowsky:* European Physical Journal E; Europhysics Letters; Lecture Notes in Physics
- *R. Miller, Herausgeber:* Advances in Coll. Surf. Sci.
- *H. Möhwald:* Chem. Phys. Mat.; Colloids and Surfaces (Herausgeber); Current Opinion Coll. Interf. Sci.; Langmuir; Nano-Letters; PhysChemChemPhys; Soft Matter

Mitgliedschaften in Fachbeiräten:
- *P. Fratzl:* Gerhardt Schmidt Minerva Zentrum für supramolekulare Strukturen; Helmholtz Programme Panel; IZFK "BIOMAT", Aachen; Photon Science Committee DESY (Chair)
- *R. Lipowsky:* Bayrische Elitenetzwerke; Institute of Theoretical Physics, CAS; Minerva Weizmann Komitee
- *H. Möhwald:* Austrian Nano Initiative (Beirat und Jury); DECHEMA Arbeitsgruppe über "Chemische Nanotechnologie"; European Colloid and Interface Society (Präsident); Fraunhofer-Institut für Angewandte Polymerforschung; German Colloid Society (Vorsitzender); Hahn-Meitner-Institut (Vorsitzender); Institut für Schichten und Grenzflächen, Forschungszentrum Jülich; Niedersächsische Hochschulevaluierungskommission; Sächsische Hochschulentwicklungskommission

Scientific Relations

National Co-operations:
The Max Planck Institute of Colloids and Interfaces (MPIKG) and the University Potsdam maintain intense and well-connected research co-operations that are among others documented by a co-operation agreement from 1995. Prof. Antonietti, Prof. Lipowsky and Prof. Möhwald are holding Honorary Professorships at the University Potsdam which reflect intensive teaching in basic studies as well as in specialized subjects. Prof. Fratzl holds Honorary Professorship at the Humboldt University Berlin. A co-operation agreement with the university and the MPIKG is in preparation. Furthermore Prof. Rabe (Department of Physics) was appointed as Foreign Scientific Member of the MPIKG in 2005.

Furthermore the "International Max Planck Research School on Biomimetic Systems" (IMPRS) is run together by the Max Planck Institute of Colloids and Interfaces and the University Potsdam. The school started within the scope of a symposium in April 2001 and will now, after successful evaluation, be continued from 2006-2012.

The institute is connected with the University Potsdam and with all Berlin universities through the German Research Foundation (DFG) priority program "Mesoscopic Composites". Also the maintainance and build-up of beamlines at the neutron- (Hahn Meitner Institute) and synchrotron radiation resources (BESSY) in Berlin and the German electron synchrotron (DESY) in Hamburg takes up big engagement. There exist co-operation agreements especially with BESSY and the Federal Institute for Materials Research and Testing for building-up and implementing a microfocus beamline.

International Co-operations:
Several research groups take part in Networks of Excellence (NoE), Marie Curie and Specific Target Research Projects (STREP) within the framework of European programs, especially the 6th framework program of the EU. In total there are six EU projects within the 6th framework program at the MPIKG. Further information is available under *www.biomimeticsystems.de* and *www.biomics.de*.

Beyond the collaborations described there exist bilateral and co-operation projects under assistance of the European Space Agency (ESA), the German Academic Exchange Service (DAAD), German Israel Foundation (GIF) for Scientific Research and Development, VW- and Zeitstiftung in France, Bulgaria, Italy, Israel, Denmark and Switzerland. Clinically oriented bone research is carried out in close collaboration with the Ludwig Boltzmann Institute of Osteology in Vienna (Austria).

In addition the MPIKG coordinates a German-French Collaborative Research Group which consists apart from all departments of the institute of five German and eight French groups. The project is jointly funded together by the DFG, CEA and CNRS. Please find further information under *www.mpikg.mpg.de/crg*.

Moreover the department of interfaces has established together with the Chinese Academy of Science an International Joint Laboratory in Beijing and a Joint Laboratory with the National Institute for Materials Science in Tsukuba (Japan).

Also the projects "Plant Cell Wall" and "ENERCHEM", funded by the strategic innovation funds of the Max Planck Society have been successfully started in 2004.

Co-operations with Industry, Application Contracts, Spin-Offs:
Among many industry contacts co-operations with well-defined targets have been with Clariant GmbH, Degussa AG and Schering AG. At present the MPIKG upholds 20 patents. In the period from 1993-2000 six spin-offs could be launched: Capsulution Nanoscience AG, Colloid GmbH, Nanocraft GmbH, Optrel, Riegler & Kirstein and Sinterface. Moreover a Junior Research Group "Nanotechnology for Life Science" has been established together with the neighbouring Fraunhofer Institute for Applied Polymer Research.

Editorial Boards:
Scientists serve as reviewers and advisors for many journals. Therefore listed are only activities as editor and member of an editorial board.

- *M. Antonietti:* Chem.Mater.; Coll.Polym.Sci.; Langmuir; Macromolecular Journals of VCh; Nach.Chem.Lab.Tech.; New J.Chem.; New Rheol. J.; Prog.Polym.Sci.; Rev.Mol.Biotech.; Small; Soft Matter

- *P. Fratzl:* J. Struct. Biol.; Calcif. Tissue Int.

- *R. Lipowsky:* European Physical Journal E; Europhysics Letters; Lecture Notes in Physics

- *R. Miller:* Advances in Coll. Surf. Sci. (Editor)

- *H. Möhwald:* Chem. Phys. Mat.; Colloids and Surfaces (Editor); Current Opinion Coll. Interf. Sci.; Langmuir; Nano-Letters; PhysChemChemPhys; Soft Matter

Memberships in Advisory Boards:
- *P. Fratzl:* Gerhardt Schmidt Minerva Center on Supramolecular Architectures; Helmholtz Programme Panel; IZFK "BIOMAT", Aachen; Photon Science Committee DESY (Chair)

- *R. Lipowsky:* Bavarian Networks of Excellence; Institute of Theoretical Physics, CAS; Minerva Weizmann Committee

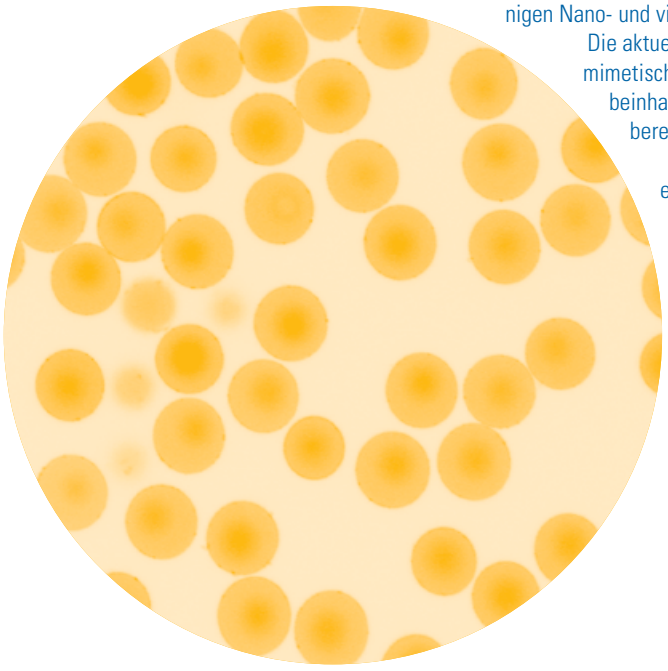
- *H. Möhwald:* Austrian Nano Initiative (Board and Jury); DECHEMA working group on "Chemical Nanotechnology"; European Colloid and Interface Society (President); Fraunhofer Institute of Applied Polymer Research; German Colloid Society (President); Hahn Meitner Institute (President); Institute of Thin Films at FZ Jülich; Lower Saxonian University Evaluation Committee on Physics; Saxonian University development committee

International Max Planck Research School (IMPRS) on Biomimetic Systems

Graduate Programs on Biomimetic Systems (BioMics)
Das Max-Planck-Institut für Kolloid- und Grenzflächenforschung (MPIKG) beteiligt sich an zwei Graduiertenprogrammen über „Biomimetische Systeme". Zum einen koordiniert das Institut gemeinsam mit der Universität Potsdam seit 2000 die „Internationale Max Planck Research School (IMPRS) on Biomimetic Systems", die eine weitere Förderungszusicherung bis zum Jahr 2012 erhalten hat. Zum anderen leitet das MPIKG das European Early Stage Training (EST), das aus einem Netzwerk von sechs europäischen Gruppen besteht.

Zusammen mit seinen Partnern bietet das Institut ausländischen und deutschen Studenten der Physik, Chemie, Biologie und Materialwissenschaften ein neues und interdisziplinäres Lehr- und Forschungsprogramm über „Biomimetische Systeme" an. Hauptziel des Graduiertenprogramms ist es, Grund legende Kenntnisse in den Bionanowissenschaften zu vermitteln und damit eine fachübergreifende Ausbildung anzubieten. Der Lehrplan muss daher eine sorgfältige Auswahl an Themenbereichen anbieten können und versuchen, die vorhandenen Sprachbarrieren zu überwinden. Die auf Englisch gehaltenen Kurse und Seminare werden von international renommierten Dozenten des jeweiligen Forschungsgebietes gehalten.

Biomimetische Systeme sind Modellsysteme, mit denen man bestimmte biologische Zusammenhänge nachahmen kann. Diese sind sehr komplex und weisen innerhalb unterschiedlicher Längenskalen viele Ebenen der Selbstorganisation auf. Das Graduiertenprogramm am MPIKG erforscht biomimetische Systeme im Bereich supramolekularer und kolloidaler Größenordnungen. Diese werden hauptsächlich durch die innere Architektur von Zellen inspiriert, enthalten viele, aus Ionen und kleinen Molekülen aufgebaute Nano-Strukturen und weisen lineare Dimensionen zwischen einigen Nano- und vielen Mikrometern auf.



Die aktuelle Forschung über biomimetische Systeme am MPIKG beinhaltet folgende Themenbereiche:

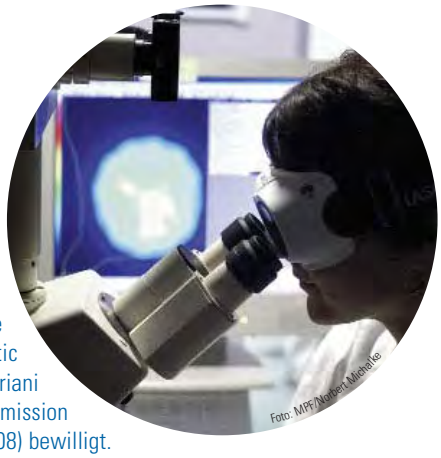
Wasserstruktur; Polyelektrolyte und andere wasserlösliche Polymere; flexible auf Lipiddoppelschichten basierende Wasserkompartimente; Diblock-Copolymerschichten und Polyelektrolyt-Multischichten; Membranfusion, aktiver Transport von molekularen Motoren; Biomineralisation und Knochen.

Während der letzten Jahre stieß die Forschung über biomimetische Systeme auf ein überaus großes, weltweites Interesse. 1999, als die Internationale Max Planck Research School (IMPRS) on „Biomimetic Systems" ins Leben gerufen wurde, war der Begriff der Biomimetik nur einer kleinen Expertengruppe bekannt. Suchmaschinen wie Google hätten zu diesem Zeitpunkt keine nennenswerten Ergebnisse aufweisen können. Dagegen hat das Wort „biomimetisch" zu Beginn des Jahres 2005 eine Popularität erlangt, die bis in die Werbung und den Film reicht. Aufgrund dieser rasanten Entwicklung zeigt Google heute mehr als 160.000 Ergebnisse bei Sucheingabe an. Dabei steht die IMPRSchool an sechster Stelle; gibt man „Biomimetische Systeme" ein, erscheint sie sogar als Erstes. Zudem erwähnenswert ist, dass der Name der Schule gewählt wurde, bevor die „Systembiologie" zu einem so genannten „Trendbegriff" in den Lebenswissenschaften wurde.

International Max Planck Research School
Der Antrag für die Internationale Max Planck Research School (IMPRS) on "Biomimetic Systems" wurde 1999 von Prof. Reinhard Lipowsky eingereicht und vom Präsidenten der Max-Planck-Gesellschaft für einen Zeitraum von sechs Jahren (2000-2006) bewilligt. Die ersten Studenten begannen im Herbst 2000, die ersten Promotionen wurden im Jahr 2003 erfolgreich absolviert. Von 2000 bis 2003 bestand die IMPRS aus sieben Partnergruppen, davon drei am MPI für Kolloid- und Grenzflächenforschung und vier an der Universität Potsdam. Die im Jahr 2003 am MPI eröffnete vierte Abteilung „Biomaterialien" etablierte zudem eine weitere Gruppe.

Im Frühling 2004 wurde die Schule evaluiert und positiv beurteilt, so dass eine Fortsetzung der Förderung von 2006-2012 genehmigt wurde. Im Wissenschaftspark Golm werden sich zwei neue Gruppen an der Universität Potsdam, zwei am Fraunhofer-Institut für Biomedizinische Technik IBMT und eine am Fraunhofer-Institut für Angewandte Polymerforschung IAP beteiligen. Drei weitere Gruppen werden an der Humboldt Universität zu Berlin etabliert mit Standort Berlin-Adlershof. Über ein Telekonferenzsystem, das auch für Vorlesungen benutzt werden kann, sind die Gruppen miteinander vernetzt.

Die Förderung erhält die IMPRSchool von der Max-Planck-Gesellschaft und dem Land Brandenburg. Diese fließt größtenteils in Form von Stipendien für Doktoranden in die



Schule. Zusätzlich dazu werden Mittel für die Organisation von IMPRS Workshops, Kolloquien und den Aufenthalt von Gastdozenten zur Verfügung gestellt. Insgesamt beträgt die zusätzliche Förderung durch die Max-Planck-Gesellschaft 2,6 Millionen Euro.

Die Rekrutierung von neuen Doktoranden wird von jeder IMPRS-Gruppe selbst durchgeführt. Darüber hinaus kann jeder interessierte Student die Bewerbungsunterlagen von der schuleigenen Webseite herunterladen. Über die Homepage und verschiedene Print- und elektronische Medien können zudem offene Stellen eingesehen werden.

Um mit anderen Institutionen konkurrieren zu können, wurde ein schnelles und unbürokratisches Zulassungsverfahren eingerichtet, wobei die deutschen und ausländischen Studenten zunächst für eine Probezeit von sechs Monaten akzeptiert werden. Zurzeit studieren ungefähr 30 Doktoranden an der IMPRS. Jeder dieser Studenten wird in eine Forschungsgruppe integriert, die Ausbildung von einem kleinen Komitee, bestehend aus Arbeitsgruppenleiter, Koordinator und Abteilungsleiter überprüft. Die Leitung der IMPRS erfolgt durch den Sprecher Prof. Lipowsky und den Programmkoordinator Dr. Valleriani. Weiterführende Informationen über die IMPRS on "Biomimetic Systems" und über die damit verbundenen Lehrveranstaltungen erhalten sie unter *www.imprs.de.*

Fig. 1: Europakarte mit den als gelben Punkten symbolisierten Partnern des EST Netzwerks

European Early Stage Training Network

2003 wurde der Antrag für das Early Stage Training (EST) Network on "Biomimetic Systems" von Prof. Lipowsky und Dr. Valleriani eingereicht und von der Europäischen Kommission für einen Zeitraum von vier Jahren (2004-2008) bewilligt. Dies ist umso erfreulicher, da in den physikalischen Wissenschaften nur vier Anträge von insgesamt 100 angenommen wurden. Die ersten Studenten haben bereits im September 2004 ihre Arbeit aufgenommen.

Das EST Netzwerk besteht größtenteils aus den Gruppen der IMPRS (drei am MPIKG, drei an der Universität Potsdam). Dazu kommen Arbeitsgruppen am Niels-Bohr-Institut in Kopenhagen, der Universität Düsseldorf, der University of Edinburgh, der Technischen Universität Leoben, dem Institute of Bioengineering in Milano und der CNRS Toulouse **(Fig. 1)**.

Das Netzwerk wird durch die Europäische Union mit einer Summe von insgesamt 3,6 Millionen Euro in Form von Zuschüssen für die Doktoranden unterstützt. Die Rekrutierung von Studenten erfolgt genauso wie bei der IMPRS. Zudem können über die Homepage und verschiedene Print- sowie elektronische Medien offene Stellen eingesehen werden. Das Netzwerk wird vom Koordinator Prof. Lipowsky und dem Projektmanager Dr. Valleriani geleitet. Detaillierte Informationen über das Early Stage Training Network on "Biomimetic Systems" erhalten sie unter *www.biomimeticsystems.org.*

Ausblick

Die Mitglieder der IMPRS beabsichtigen, an der Universität Potsdam und der Humboldt Universität zu Berlin einen neuen Masterstudiengang „Biomimetische Systeme" einzurichten. Zusammen mit der bereits bestehenden IMPRS wird dieser Masterstudiengang ein gesamtes Graduiertenprogramm über „Biomimetische Systeme" anbieten. Darüber hinaus soll ein einjähriger Intermediate-Kurs für Bewerber eingerichtet werden, die hoch motiviert sind, sich mit „Biomimetischen Systemen" zu beschäftigen, aber noch Zusatzkenntnisse benötigen.

Reinhard Lipowsky und Angelo Valleriani

International Max Planck Research School (IMPRS) on Biomimetic Systems

Graduate Programs on Biomimetic Systems (BioMics)

The MPI of Colloids and Interfaces is involved in two graduate programs on "Biomimetic Systems". First, it has established, together with the University of Potsdam, an International Max Planck Research School (IMPRS) on this topic which was launched in 2000 and has recently been approved for continuation until 2012. Second, the MPI also coordinates a European Early Stage Training (EST) network which includes six partner groups in Europe.

The MPI of Colloids and Interfaces offers, together with its partner groups, a new and interdisciplinary curriculum on "Biomimetic Systems" for foreign and German students from physics, chemistry, biology, and materials science. One major goal of this curriculum is to provide a common basis of knowledge for the bionano sciences which transcend the traditional boundaries between the different disciplines. This implies that the curriculum must provide a careful selection of topics and that each course must make an effort in order to overcome the usual language barriers. All courses and seminars are in English and given by lecturers who are active researchers in the field.

Biomimetic systems are model systems by which one can mimic certain aspects of biological systems. The latter systems are complex and exhibit many levels of self-organization over a wide range of length scales. The graduate programs at the MPI of Colloids and Interfaces are focused on biomimetics at the supramolecular or colloidal levels for which the interior architecture of cells provides the main source of inspiration. These levels contain many different nanostructures that are built up from ions and small molecules and which attain linear dimensions between a few nanometers and many micrometers.

Current research on biomimetic systems at the MPI of Colloids and Interfaces includes the following topics: Water structure; polyelectrolytes and other water soluble polymers; flexible microcompartments based on lipid bilayers, diblock copolymer bilayers, and polyelectrolyte multilayers; membrane fusion; active transport by molecular motors; active stress generation in plants, collagen and connective tissue, bio-mineralization and bone.

During the last couple of years, research on biomimetic systems has become a hot topic around the world. In the year 1999, when the International Max Planck Research School (IMPRS) on these systems has been proposed, the term "biomimetic" was known only to a small group of experts, and search engines such as Google would not return any significant number of results. Now, at the beginning of 2005, "biomimetic" has become a popular term that is mentioned even in movies and advertisements, and Google returns more than 160.000 results for it! In fact, our IMPRSchool is currently returned as the sixth result for "biomimetic" and as the first result for "biomimetic systems". It is also worth mentioning that the name for our school was chosen before "systems biology" became a fashionable topic in the life sciences.

International Max Planck Research School

The proposal for the International Max Planck Research School (IMPRS) on "Biomimetic Systems" was initially submitted by Reinhard Lipowsky in 1999 and was approved by the President of the Max Planck Society for a six-year period from 2000 until 2006. The first students were accepted in fall 2000 and the first doctoral degrees were granted in 2003. Until 2003, the IMPRS consisted of seven partner groups including the three departments at the MPI of Colloids and Interfaces and four groups from the University of Potsdam. In 2003, the fourth department on "Biomaterials" was established at the MPI and started to participate in the school.

The performance of the school was evaluated by an on-site panel in spring 2004 and our continuation proposal was approved for a second funding period from 2006 until 2012, during which several groups will join the school: Two groups from the University of Potsdam; three groups from Humboldt University Berlin; one group from the Fraunhofer Institute for Applied Polymer Research IAP; and two groups from the Fraunhofer Institute for Biomedical Engineering IBMT, which will move to the Science Park in Potsdam-Golm in 2006. The groups from Humboldt University are located in Adlershof, Berlin and will be connected by teleconferencing systems which will also be used for telelecturing.

The IMPRSchool is supported by central funds from the Max Planck Society and by special funds from the state of Brandenburg. Most of this funding comes in the form of stipends for doctoral students. Additional funds are available for the organization of IMPRS workshops and colloquia and for the invitation of guest lecturers. The total amount of additional funding provided by the Max Planck Society for the IMPRSchool is 2.6 Million Euro.

Each IMPRS group actively recruits new graduate students for the school. In addition, the school has a centralized recruitment procedure that is primarily based on its website where a complete application package is provided for download. Available positions are advertised via this website and posted in various print and electronic journals.

A fast and non-bureaucratic admission procedure has been installed which is necessary in order to compete with other institutions for the best students. Both foreign and German students are first accepted for a trial period of six months. At present, about 30 doctoral students are enrolled in the IMPRS program. After enrolment, each student joins a research team. Their career development is monitored by a small committee consisting of the team leader, the coordinator of the school and the head of the department. The IMPRS is managed by its speaker Reinhard Lipowsky and its program coordinator Angelo Valleriani.

More detailed information about the International Max Planck Research School on "Biomimetic Systems" such as course programs for each semester can be found on its website at *www.imprs.de*.

European Early Stage Training Network

The proposal for the Early Stage Training (EST) network on "Biomimetic Systems" was submitted in 2003. The European Commission approved it for a four-year period from 2004 until 2008. For these funds the competition was rather strong: in the physical sciences, only four proposals out of about 100 have been accepted. The first EST students started to work in September 2004.

The EST network consists of most groups from IMPRS (three departments of the MPI, three groups from the University of Potsdam) as well as additional research groups from the Niels Bohr Institute in Copenhagen, the University of Düsseldorf, the University of Edinburgh, the Technical University in Leoben, the Institute of Bioengineering in Milano, and CNRS Toulouse, **see Fig.1.**

Fig 1: A map of Europe with the partners of the EST network indicated by yellow dots.

The network is supported by the European commission in the form of grants for doctoral students. The total amount of these grants is 3.6 Million Euro. The recruitment of students for EST is done in the same way as for IMPRS. Available positions are advertised via the website of the network and posted in various print and electronic journals. The network is managed by its coordinator Reinhard Lipowsky and its project manager Angelo Valleriani.

More detailed information on the Early Stage Training Network on "Biomimetic Systems" can be found on its website at *www.biomimeticsystems.de*.

Outlook

The members of the IMPRSchool intend to establish a new Master's course on "Biomimetic Systems" at the University of Potsdam and at the Humboldt University, Berlin. Together with the existing IMPRSchool, this Master's course will represent a complete graduate program on "Biomimetic Systems".

In addition, we would like to install an intermediate one-year course for those applicants to our IMPRSchool and EST network who are highly motivated to work on "Biomimetic Systems" but need additional training before they can do so.

Reinhard Lipowsky and Angelo Valleriani

Presse- und Öffentlichkeitsarbeit

Mit der Presse- und Öffentlichkeitsarbeit will das Max-Planck-Institut für Kolloid- und Grenzflächenforschung über seine Arbeit sowie seine Ergebnisse in Lehre und Forschung informieren und so ein eigenständiges, positives Image und Vertrauen schaffen. Gleichzeitig soll dazu beigetragen werden, eine Brücke von der Lehr- und Forschungsstätte in die Öffentlichkeit zu schlagen und Impulse aufzunehmen. Ein Hauptziel ist es, unsere aktuelle Forschung in das Bewusstsein der allgemeinen Öffentlichkeit, der Politik, der Presse, unserer Kooperationspartner, zukünftiger Studenten, ehemaliger Institutsangehöriger sowie der internen Gemeinschaft zu bringen und ihre Akzeptanz sowie Anerkennung in der Gesellschaft zu stärken. Fach- und Publikumsjournalisten werden über das aktuelle Geschehen mit Hilfe von fundierten Nachrichten und Hintergrundwissen informiert. Regelmäßig veröffentlichen wir unseren Zweijahresbericht, eine Campus-Broschüre über den Wissenschaftspark Golm sowie Presse-Informationen, organisieren Pressekonferenzen und halten zu den Medienvertretern persönlichen Kontakt.

Neben der klassischen Pressearbeit stellt die komplette Konzeption, Organisation und Durchführung von Veranstaltungen den zweiten Tätigkeitsschwerpunkt des Referats dar. Der alljährliche Tag der offenen Türen im Wissenschaftspark Golm ist dabei einer unserer Höhepunkte. Gemeinsam mit den Max-Planck-Instituten für Gravitationsphysik und Molekulare Pflanzenphysiologie, dem Fraunhofer-Institut für Angewandte Polymerforschung sowie der Universität Potsdam bieten wir interessierten Besuchern aller Altersklassen einen faszinierenden Einblick in die Forschung. Das mannigfaltige Programm mit Führungen, Experimenten, Vorträgen und Mitmach-Aktionen bietet Jung und Alt Wissenschaft zum Anfassen und die Möglichkeit High-Tech-Technologien hautnah zu erleben. Der Tag der offenen Türen wird im Jahr 2005 am 27. August stattfinden und durch den „nanoTruck" des Bundesministeriums für Bildung und Forschung (BMBF) und der Initiative Wissenschaft im Dialog (WiD) unterstützt.

Zudem bietet das Max-Planck-Institut für Kolloid- und Grenzflächenforschung Führungen an und organisiert Vorträge an Schulen. Wir unterstützen Sie jederzeit bei auftretenden Fragen und sehen es als unsere Aufgabe an, die Bedeutung der Grundlagenforschung und der zukünftigen Entwicklungen in der Kolloid- und Grenzflächenforschung an die breite Öffentlichkeit zu transportieren.

Katja Schulze
Presse- und Öffentlichkeitsarbeit

Fotos: links J. Bergstein, rechts K. Fritze

Press and Public Relations

Public relations at the Max Planck Institute of Colloids and Interfaces serve as the interface between the scientists' work and the public. We inform you about the research results and want to create an independent, positive image and thus trust in scientific work. Simultaneously we try to bridge the gap between research institution and general public and hence get new impetus. We promote the perception of our research among the community, the press, government, corporate partners, prospective students, alumni and our own internal community. It is a matter of great importance that not only the scientific community but in fact anyone interested in modern science should have the opportunity to get an idea about the aims of our institute. Therefore we inform journalists with profound news and background knowledge about current research. To pursue this task press releases are edited, brochures – such as the biannual report or the Campus brochure are published and distributed on request and informal support is provided whenever necessary.

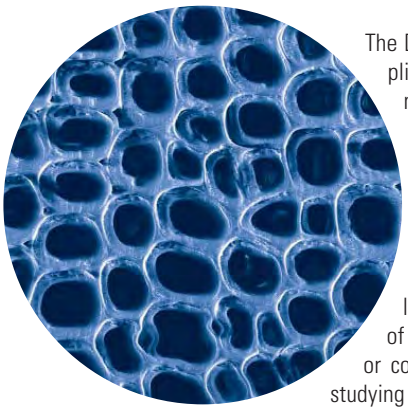
Beside classical public relations the complete conception, organisation and realisation of events is a second core theme. One of our highlights every year is the Open Day on the Research Campus Golm, which is an interesting and fun-packed day, combining demonstrations of high-tech learning facilities with hands on activities for all age groups. The Open Day 2005 will be held together with the Max Planck Institute of Gravitational Physics, the Max Planck Institute of Molecular Plant Physiology, the Fraunhofer Institute of Applied Polymer Research and the University Potsdam on August 27. There will be lab tours, popular talks and scientific demonstrations providing an excellent opportunity for everybody to experience scientific activity at first hand. The Open Day 2005 is supported by the "nanoTruck" of the Federal Ministry of Education and Research (BMBF) and the "Science in Dialogue" (WiD) initiative.

Furthermore tours through the institute as well as talks at schools are organized. We try to create awareness for the role of basic research in general, especially with regard to future developments in colloid and interface science. We also seek to show that the world of science and technology is fascinating, challenging, varied, and rewarding. Within these pages you can find the latest news from the institute as well as a more in depth look at our research.

Katja Schulze
Press and Public Relations

BIOMATERIALS

Research in the Department of Biomaterials



The Department of Biomaterials focuses on interdisciplinary research in the field of biological and biomimetic materials. The emphasis is on understanding how the mechanical or other physical properties are governed by structure and composition (see **Fig. 1**). Furthermore, research on natural materials (such as bone or wood) has potential applications in many fields. First, design concepts for new materials may be improved by learning from Nature. Second, the understanding of basic mechanisms by which the structure of bone or connective tissue is optimised opens the way for studying diseases and, thus, for contributing to diagnosis and development of treatment strategies. A third option is to use structures grown by Nature and transform them by physical or chemical treatment into technically relevant materials (biotemplating). Given the complexity of natural materials, new approaches for structural characterisation are needed. Some of these are further developed in the Department, in particular for studying hierarchical structures.

Hierarchical Structure of Natural Materials

The development of metals and alloys with increasing strength has been a constant trigger for the technical development of our societies. Interestingly, Nature does not use metals as structural materials at all. Practically all biological materials are based on polymers and polymer-mineral composites. The required mechanical performance is obtained by an intelligent structure which is hierarchical and optimised at all levels.

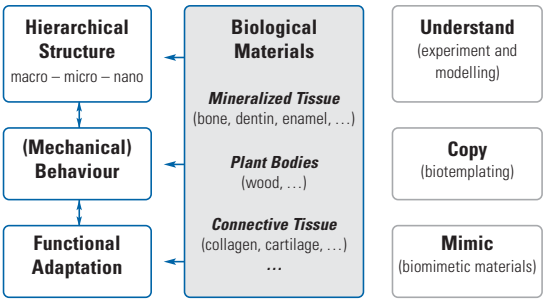


Fig. 1: General research goals in the Department of Biomaterials

Mechanical Adaptation of Biomaterials

It is also well-known that biological materials constantly adapt to changing mechanical needs. This is achieved by a strain-sensing mechanism, which in most biological systems is not fully elucidated. In the case of bone, for instance, specialized cells are thought to act as strain sensors and to be at the centre of a feed-back loop, called bone remodelling cycle, where damaged bone is removed and replaced by new material. This process is crucial for the tissue's capability of mechanical adaptation and self-repair.

New Methods for Analysis of Biomaterials

Studying hierarchical biomaterials requires state-of-the-art experimental equipment, but there is also some need for the development of new approaches. Scanning methods based on the diffraction of synchrotron radiation, as well as the technique of small-angle x-ray scattering (SAXS) are continuously developed to improve the characterization of hierarchical biomaterials. Further technical improvement is expected from a dedicated scanning set-up which is currently being installed at the synchrotron BESSY in Berlin.

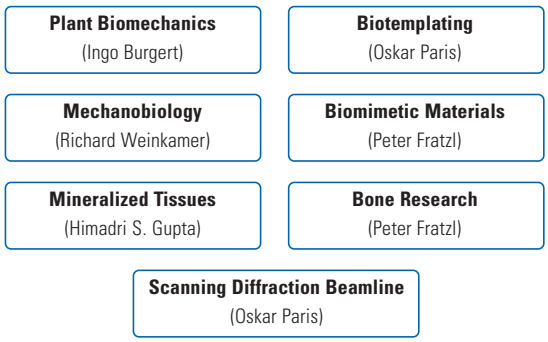


Fig. 2: Research groups in the Department of Biomaterials with respective group leaders

Research Strategy

The research on biomaterials is currently concentrated in seven research groups as sketched in **Fig. 2**. Three groups (left column in **Fig. 2**) deal with "understanding" (see **Fig. 1**) the mechanical properties of biological materials and their adaptation to external stimulus. Three more groups (right column in **Fig. 2**) concentrate on more applied goals, relating to the development of new materials, on the one hand, and to medical problems in bone research, on the other. Finally, a seventh group is dedicated to the development of a new micro-focus beamline for scanning x-ray scattering applications at the BESSY synchrotron in Berlin. More detailed goals of the different research groups are outlined below.

Plant Biomechanics

The main goals are:

- To understand plant tissue as a fibre composite in relation to its mechanical adaptation;
- To understand the nano-structure and mechanical properties of the plant cell wall;
- To obtain basic knowledge on structure-property relationships in plants for transfer to technical systems.

Mineralized Tissues

The main goals are:

- To understand how bone and related calcified tissues are designed at the micro- and nano- levels to fulfil their load-bearing and structural requirements;
- To develop a theoretical formulation that relates the mechanical properties of mineralized tissues to their structure at the sub-micron level.

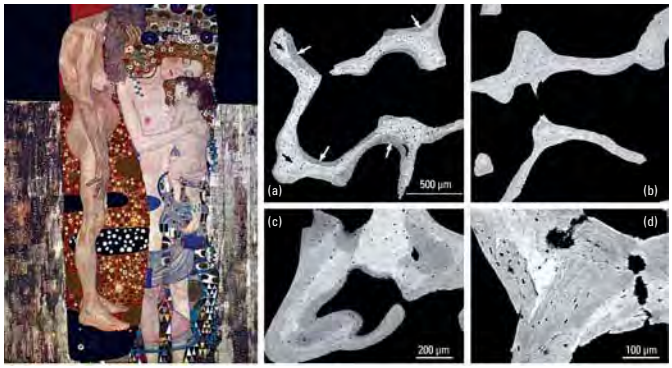
Mechanobiology
The main goals are:
- To understand and predict the adaptation of materials to mechanical requirements by means of numerical simulation;
- To improve the understanding of the biological response of natural tissues to mechanical stimulus and the associated feedback mechanisms by means of theoretical analysis.

Biotemplating
The main goals are:
- To take natural tissues as scaffolds or moulds for the creation of novel engineering materials with improved mechanical and functional properties;
- To preserve and/or replicate the hierarchical structure of the biological tissues down to the nanometer regime during the conversion process.

Biomimetic Materials
The main goals are:
- To use the building principles of natural hierarchical composites, such as bone, collagen or the plant cell wall, to improve existing materials by shaping and structuring.
- Current work includes: Biomimetic polymer-mineral composites; Designed porous scaffolds with optimised mechanical properties; Novel precious metal-based bio-nano-catalysts; synthesis of hydroxyapatite naoparticles with special shapes.

Bone and Mineral Research
This group works in close collaboration with external medical research groups and its main goals are:
- To study clinical problems related to bone material quality in various bone diseases, such as osteoporosis or brittle bone disease,
- To establish the effect of genotype on bone material in animal models and for genetic diseases,
- To develop new physical methodology for assessing bone material quality.

Scanning Diffraction Beamline
The main goals are:
- To develop a microfocus synchrotron beamline for scanning x-ray scattering applications, in collaboration with BESSY and the Federal Institute for Materials Research (BAM), the idea being to use the small-angle and/or diffraction signal to image a specimen with micrometer resolution;
- To develop high-throughput technology for online data analysis, to deal with the enormous amount of data collected in scanning diffraction applications;
- To implement a platform for the study of biological specimens (in particular cryo-sections).



Gustav Klimt (1862-1918):
Three ages of a women, 1905

(a) normal, (b) bisphosphonate, (c) parathyroid hormone, (d) NaF

Fig. 3: Various treatment strategies of osteoporosis investigated with back-scattered electron microscopy in collaboration with the Ludwig-Boltzmann Institute of Osteology in Vienna, Austria (courtesy, Dr. Paul Roschger)

Peter Fratzl
Director of the Department
of Biomaterials

Calcified Tissue Structure and Mechanics

Himadri Shikhar Gupta 26.06.1973
1991-1996: M.Sc. in Physics (Indian Institute of Technology, Kanpur, India)
1996-2000: PhD, Physics (Department of Physics and Astronomy, Rutgers, The State University of New Jersey, New Brunswick, New Jersey, USA)
Thesis: Phase Segregation and Alloying in Ni-base Superalloys: Models and Experiments
2000-2002: Postdoc, (Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria)
Since 2003: Group Leader (Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam)

Structural Adaptation and Mechanisms of Deformation in Calcified Tissues

The general aim of this group is to elucidate how the various structural features of natural calcified tissues (bone, tendon, cartilage) relate to their mechanical behavior **[1]**. Specifically, three types of tissues were addressed. (a) Mineralized cartilage, which is the crucial interface between subchondral bone and articular cartilage in articulating joints; (b) Parallel fibered mineralized collagen from tendon and bone, in order to elucidate mechanical deformation mechanisms at the fibril level; (c) And single osteons, the basic building block of compact bone, comprising layers of lamellar bone around a blood vessel. The aim was to resolve their intra-lamellar structure in terms of the orientation, size, shape and crystallographic structure of the nanometer size crystallites in relation to the mechanical properties of the lamellae.

Local Correlation of Modulus to Mineral Content at the Bone – Cartilage Interface

Patellar knee sections from human specimens were characterized mechanically and chemically, using scanning nanoindentation and quantitative backscattered electron imaging (qBEI), across the bone – calcified cartilage interface. Significantly different correlations between mineral content and elastoplastic properties were found between bone and calcified cartilage suggesting a different mineral particle – organic matrix arrangement at the fibrillar level. Quantitatively, our results are consistent with a model of thin elongated mineral particles tightly bound to an intermediate organic matrix **(Fig. 1a)**. At the tissue level, the generated two-dimensional material property maps of the elastoplastic properties **(Fig. 1b)** show that the bone cartilage interface is naturally designed as a functionally graded material, in order to minimize propagation of tissue – disrupting cracks, a finding which may have implications for biomedical engineers attempting to model the deformation and compressive behavior of articulating joints and their pathological alterations in common joint diseases like osteoarthritis **[1]**.

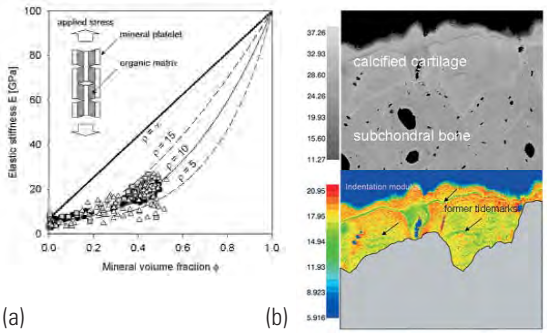


Fig. 1: (a) Comparison of the modulus–mineral relations predicted by the staggered model for ZCC with the measured cartilage nanoindentation modulus. Inset figure: schematic of the staggered model (b) Two dimensional property maps of calcium content and elastic modulus, at the bone – calcified cartilage interfaces

Fibrillar Level Deformation Mechanisms in Mineralized Tendons and Bone

For partially mineralized avian tendons for low (<1–2%) macroscopic strains, the fibril level deformation follows the applied external stress, for larger strains, an unexpected biphasic behavior is observed, where a portion of the fibrils relax back to their unstressed state while the remainder elongate to much larger strains, while maintaining macroscopic cohesion **(Fig. 2b)**. By combining the results with fractographic analysis using scanning electron microscopy, we find that the mineralized tendon consists, at the micrometer level, of a heterogeneously mineralized group of unmineralized and fully mineralized fiber bundles of 2 – 4 micron diameter. Our results are interpreted in terms of two-fiber composite model **(Fig. 2b)**, inset) in which the highly mineralized fibers account for the macroscopic stiffness and the lowly mineralized fibers the high work to fracture **[2]**. In contrast, our more recent work on parallel fibered bovine bone from the periosteum shows that the fibrillar strain in bone tissue is continuously proportional to that of the macroscopic strain. Surprisingly, this 1 – to – 1 correspondence is maintained in the inelastic regime, where mechanisms like microcracking of fibrils and fibril-matrix decohesion may be important **(Fig. 2c)**. The response of fibrils to stress and strain relaxation is the subject of current work.

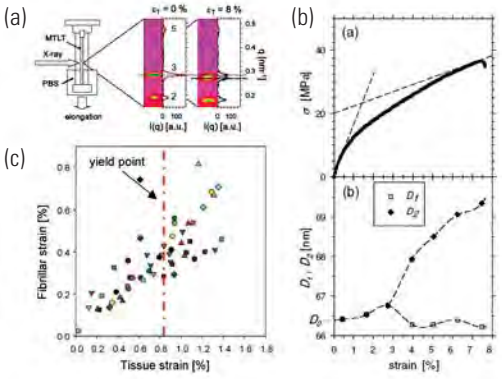


Fig. 2: (a) Principle of in-situ tensile testing combined with synchrotron X-ray diffraction. (b) Fibrillar level change in collagen D-periodicity to applied external strain in mineralized tendon. (c) Fibrillar level strain in bone compared to applied tissue strain

Mineral Particle Orientation and Nanomechanical Properties in Single Bone Lamellae

By combining µ-focus synchrotron X-ray diffraction and scattering (SAXS (small angle X-ray scattering) and WAXD (wide angle X-ray diffraction); **Fig. 3**) with texture measurements, we show quantitatively that the mineral platelets change their orientation, continuously, across a single lamella, consistent with the twisted rotated plywood model proposed by Wagner and Weiner. Indeed, our results permit, for the first time, reconstruction of the full 3D distribution of platelet and crystallographic orientations at a single point of 1 micron^3 volume. In combination with Raman microscopy measurements, our results will be used for a complete picture of the organic – inorganic structural and chemical composition within single bone lamellae.

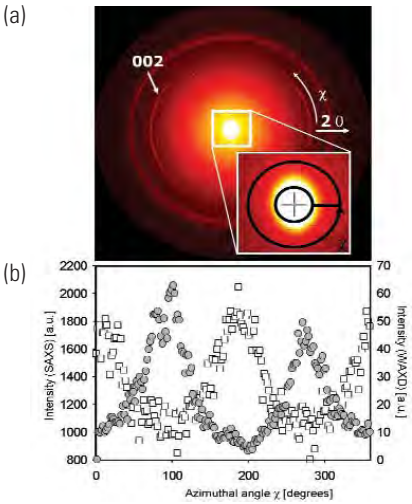


Fig. 3: (a) 2D MAR CCD detector image of osteonal bone, showing central SAXS signal and peripheral WAXD rings from (002) and (310) reflections (b) Integrated azimuthal SAXS and WAXD intensity profiles, with complementary information.

Scanning nanoindentation (500 µN, 20 µN/s) combined with backscattered electron imaging was used to build two – dimensional material property maps of the mechanical properties of human osteons **(Fig. 4a)**. It was found that each 5 micron wide lamellar unit consists of an alternately stiff and ductile layer, arising from a combination of the fiber orientation and mineral content **(Fig. 4b)**. This natural mechanism reproduces, at a lower length scale, similar results found for human dentin, and is likely to have a similar biological function **[3]**.

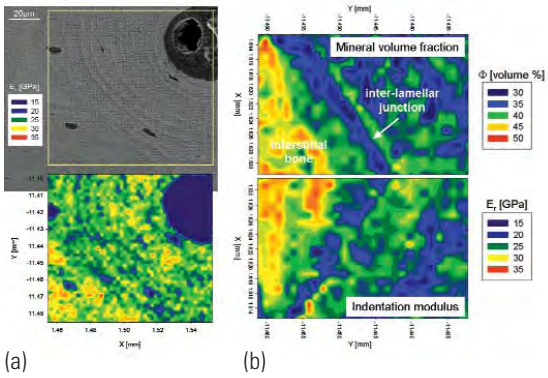


Fig. 4: (a) Two-dimensional map of elastic modulus around an osteon, showing the lamellar variation in mechanical properties (b) Detailed image of the edge of another osteon, where the correlation between mineral conten (top) and elastic modulus (bottom) is shown.

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Bone and Mineral Research

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Bone is a hierarchical material and its mechanical properties depend on its structure at all levels of hierarchy. As a consequence, bone fragility may result from defects in any of the hierarchical levels. This concerns bone diameter and bone mass, as well as its internal architecture. At the lowest structural level, bone fragility could result from modifications in the collagen-mineral composite which constitutes the bulk of bone material. While bone mass is routinely evaluated in clinical practice, the quality of the bone material is much more difficult to assess. The general aim of this research group, which is constituted by researchers from the MPI as well as from the Ludwig Boltzmann Institute of Osteology in Vienna, a medical bone research institution, is to study changes in bone material quality with disease and treatment.

The main difficulty in this task is the extreme heterogeneity of the tissue which due to the permanent remodelling of bone. Old bone is being removed and new osteoid is added. This osteoid then mineralizes and the mineral content increases over several months. As a consequence, newly formed bone is less mineralized than old bone, as visualized, e.g., by back-scattered electron imaging in **Fig. 1**. In addition, mineral particles increase in thickness T from newly formed to mature bone **(Fig. 1)**.

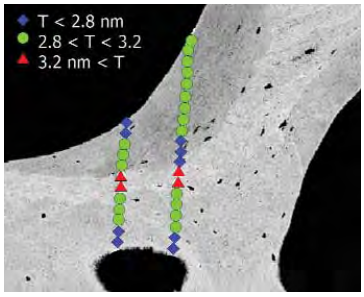

Fig. 1: Backscattered electron image of a section of human trabecular bone (from an iliac crest biopsy). The grey scale indicates mineral content, older bone being lighter than young bone. The black regions correspond to bone marrow and to cells embedded in bone. Young bone also has smaller mineral particle thickness T, as measured by small-angle scattering on the same section.

The consequence of this heterogeneity is that bone sections (usually from biopsies) have to be investigated in a position resolved way. The research group is developing and validating a number of techniques which all allow a resolution in the micron range and can be combined to study the same specimen: light microscopy to characterize cells and soft tissue components, backscattered electron imaging to determine mineral density distributions **[1]**, scanning small- and wide angle diffraction with synchrotron radiation to characterize mineral particles (see report about the beamline at BESSY) and scanning nanoindentation to study local variations of mechanical properties. The latest addition is Raman spectroscopic imaging, mainly to get information on the status of the organic component in fully mineralized bone.

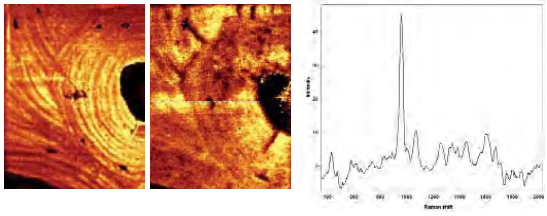

Fig. 2: (a) Fluorescence image and (b) Phosphate contrast of an osteon and (c) an example of a Raman spectrum from the pointed region.

Raman spectroscopy uniquely provides non-destructive, quantitative information simultaneously on the mineral and the protein matrix and is sensitive to local environmental effects, such as change in mineral substituents or protein secondary structures. Raman microspectroscopy and imaging provide molecular structure information with a spatial resolution in the micrometer range. The goal is to extract chemical information and spatial distribution without any prior information about the composition of the object being imaged. **Fig. 2** shows fluorescence and phosphate contrast Raman images of an osteon, that is, of the basic unit of compact bone consisting of a blood vessel surrounded by lamellar bone. The lamellar structure is clearly visible in the fluorescence image, but the phosphate distribution shows that mineral is homogeneously distributed across the lamellae.

Combinations of these approaches were used to study various cases of disease and treatment, both in animal models and in patient studies. Some examples are given below

Alkaline Phosphatase Deficiency

Tissue non-specific alkaline phosphatase (TNALP) is expressed in many tissues and is supposed to play an important role in bone mineralization. Reduced activity of this enzyme may lead to hypophosphatasia, a rare metabolic disorder. In order to get more insight into the importance of TNALP on the development of bone material, a transgenic mouse model deficient in this enzyme was studied **[2]**. A first interesting observation was that the texture of the bone material (that is, the alignment of the collagen fibrils and mineral particles) has a systematic variation along the cortical bone of the femur (see **Fig. 3**).

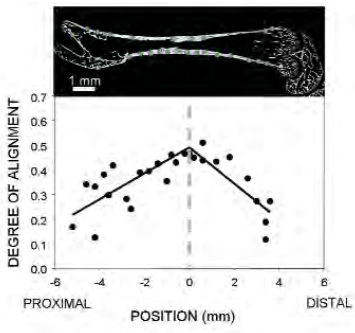

Fig. 3: degree of alignment of mineral particles in mouse femur (from [2]).

This orderly arrangement, which improves the bending strength of the femur, is lost in the TNALP deficient mice **(Fig. 4)**

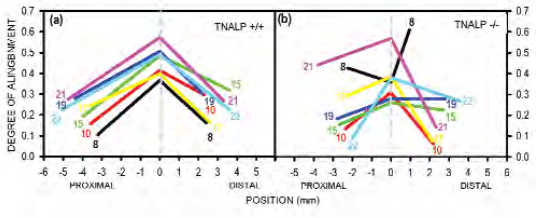

Fig. 4: Changes in the material texture with age and with TNAP status in mouse femur (from [2]).

Fra-1 Overexpression

Overexpression of Fra-1 results in an elevation of the number of mature osteoblasts, the bone forming cells. Bone material quality was studied in transgenic mice showing such an overexpression. While these mice are normal at birth, a dramatic increase in bone volume, well above normal levels (five fold!) occurs during maturation (see **Fig. 5**). Most interestingly, the material micro- and nano-structure did not show any obvious modifications which might encourage efforts to develop therapies based on Fra-1 against pathological bone loss **[3]**.

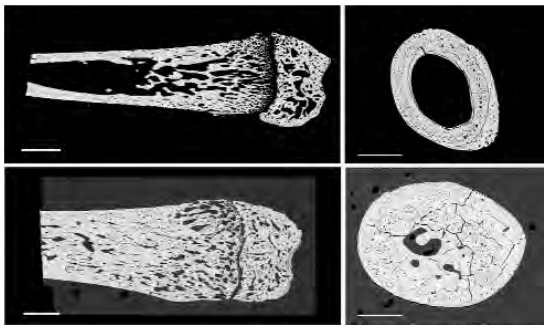

Fig. 5: Mineral distribution in femur or normal mice (top) and of transgenic mice with Fra-1 overexpression (bottom row) [3].

Vitamin D Receptor Overexpression

Vitamin D plays an important role in calcium homeostasis and in bone development. Bone material quality was investigated in transgenic mice with an overexpression of vitamin D receptors. The mineralization profile in these mice was more homogeneous than usual, however with normal structure at the nanometer level, a result which correlates well with the increased stiffness of bone in these animals **[4]**.

Osteoporosis Treatment with PTH

In a large international collaboration, the effect of parathyroid hormone (PTH) treatment on bone material was investigated for osteoporosis patients. Biopsies before and after treatment were investigated and showed a dramatic change in the mineralization pattern **[5]**, as visible in **Fig. 6**.

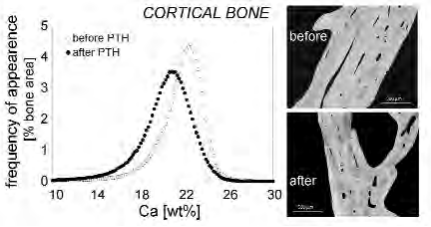

Fig. 6: The mineral density distribution is considerably broadened after PTH treatment [5].

Pycnodysostosis

Pycnodysostosis is a rare genetic disease where patients are deficient in the enzyme cathepsin K, which is essential to degrade the bone matrix. As a consequence, bone remodelling is strongly disturbed. Biopsies from patients showed a disordered bone matrix, since a proper adaptation is not possible anymore. These results have importance beyond the actual disease, since cathepsin K inhibitors are currently investigated as possible drugs against osteoporosis **[6]**.

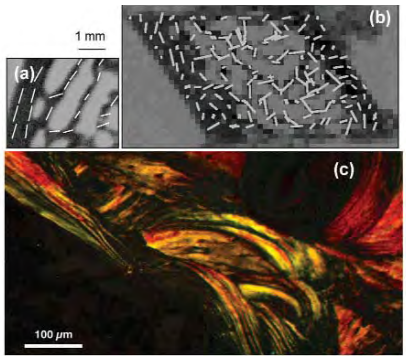

Fig. 7: Mineral particle orientation shown by white bars in (a) normal bone and (b) pyknodysostosis. (c) Disordered collagen arrangement revealed by polarized light (from [6]).

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Mechanobiology and Pattern Formation

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The premise of mechanobiology is that biological systems can detect mechanical stimuli and subsequently react to them. Examples for mechanobiological systems are plants and bone. We focused our attention to the remodeling process in trabecular bone (see **Fig. 1**) to understand how this process is controlled via the action of specialized cells.

In interplay of bone resorbing osteoclasts and bone depositing osteoblasts, living bone remodels its architecture in response to mechanical loading. This ability for adaptation is thought to occur in a remodeling process, where bone material is removed where the local mechanical stimulus is low and added where it is high (Wolff-Roux law). Implementing this law in a computer model and using finite-element methods (FEM), it was successfully demonstrated that optimized trabecular architecture emerges, is maintained and adapts to varying loads. However, concerning this mechanical feedback-loop the most basic questions are still unanswered like: to what mechanical stimulus cells are reacting to and in which way do they react? What is the connection between dysfunctions of the control system and bone diseases like osteoporosis? With computer simulations we can study the effect of different realizations of the control systems on the time evolution of bone microstructure **[1]**. An approximate, but fast algorithm to assess the local mechanical load in the network-like structure of trabecular bone was employed. The obtained result was then fed back into the local probabilities for bone deposition/resorption. This unknown law – we termed it remodel law – which couples the mechanical stimulus to the cell action is the basic unknown. The approximate treatment of the mechanics allows us to study the architectural evolution of trabecular bone inside a vertebra in a multitude of different settings and remodel laws over a human life time and beyond.

In our model the architecture of the trabecular bone inside a human vertebra is mapped on a simple cubic lattice with occupied sites, corresponding to bone, and unoccupied sites, corresponding to marrow. Such lattice models are successfully used for different problems in physics when geometry plays an important role **[2]** and the microstructures e.g., in alloys are often amazingly similar to the ones found in bone **[3]**. We assume that the local volume change is the mechanical stimulus the cells are responding to. As remodel laws simple relations between stimulus and deposition probability have been implemented, e.g., linear relations, step-functions or combinations of them as proposed in the bone literature.

Starting with a homogeneous configuration of high bone volume fraction, a network-like structure emerged with horizontal and vertical trabeculae **(Fig. 1)**.

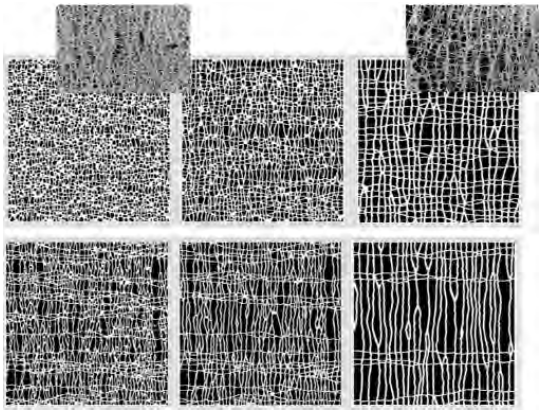

Fig. 1: Snapshots of two-dimensional simulations with time proceeding from left to right. Bone matrix is indicated white, marrow black. Simulations in the bottom row were performed with a reduced sensitivity of bone-depositing cells to the mechanical stimulus. For both simulations the starting configuration was a random arrangement of occupied sites of high volume fraction. The smaller, upper insets show for comparison micrographs of trabecular bone inside a human vertebra: young and healthy on the left, old and osteoporotic on the right.

In all simulations the bone volume fraction reached a steady state value. The architecture, however, coarsened, i.e., the trabecular number decreased while the trabecular thickness increased **[1]**. Since vertical trabeculae thickened faster, an anisotropy favoring the main loading direction became more pronounced. A small reduction in the sensitivity of the osteoblasts resulted in a decreased bone volume fraction and a deterioration of the microstructure from a mechanical point of view (**Fig. 1**, bottom row). These features of a reduced bone volume, a coarser structure and a more distinct anisotropy between vertical and horizontal trabeculae are observed also in osteoporotic patients.

While **Fig. 1** shows the effect of changes in the model parameter while the remodel law is fixed, **Fig. 2** compares the outcome of three-dimensional simulations using different remodel laws **[4]**.

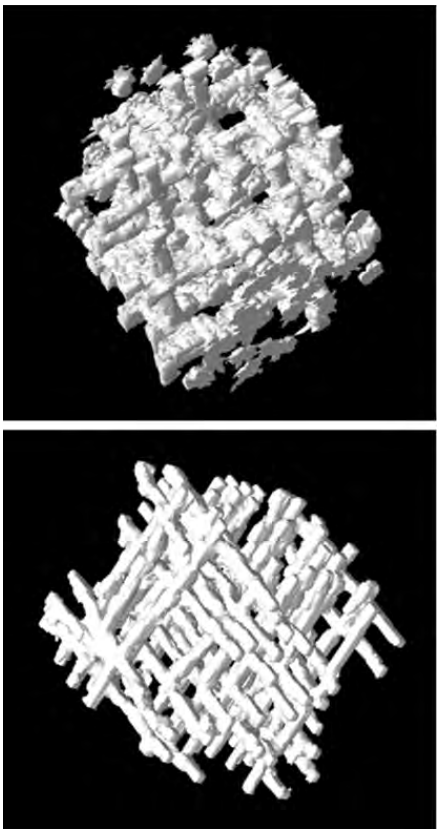

Fig. 2: Comparison between the three-dimensional configuration obtained by two different remodel laws: a linear relation between stimulus and deposition probability (top), a step-function corresponding to on/off-control (bottom).

The morphological differences can be quantified using either standard bone morphometry or more sensitive measures which we have developed. An influence of the remodel law can be observed not only in the morphology, but also in the effect of perturbations on the system. As an example we studied the effect of an increased turnover rate, i.e., a higher activity of the cells as observed, for instance, in women at menopause. In this case we obtained the result that depending on the remodel law the bone volume fraction either decreases or remains unaffected **[4]**. Interestingly, also in the case of an unchanged volume fraction the trabecular morphology coarses rapidly. All these observations have to be evaluated in comparison to data on real bone using advanced imaging techniques (e.g., μCT) and to outcomes from clinical studies. Based on this comparison we should be able to draw conclusions about the law governing bone remodeling.

As a final demonstration and future outlook of how this connection between simulation and experiments on bone works utilizing the "omniscience" in simulations, **Fig. 3** shows the age distribution in trabecular bone: younger bone is preferentially at the surface, older bone inside the trabeculae, as expected.

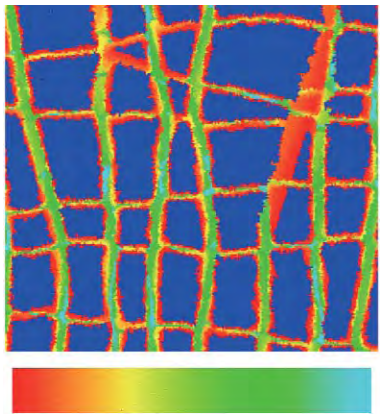

Fig. 3: A small cutout of the two-dimensional system showing the result of a representative simulation. The colors correspond to the time when the bone element was deposited. Red denotes the youngest (= most recently deposited) bone, turquoise the oldest bone. In real bone recently deposited bone can be detected as being less mineralized than older one.

Entering here the discussion about the possible creation of new trabeculae, the simulation demonstrates the existence of trabeculae consisting only of very young bone, but which were definitely not newly created. Since age corresponds to a higher mineralized state in real bone, this distribution is also experimentally accessible. A histogram of the bone mineral density was actually shown to be a sensitive fingerprint discriminating healthy and diseased bone.

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Plant Biomechanics – Structure-Function Relationships at the Micro- and Nanoscale

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Plants are hierarchically organised and possess remarkable mechanical properties. The unique performance of plant biomaterials is based on sustained optimization processes of the organism, which become obvious in the shape of the organs and in the adapted molecular structure. To meet the natural demands of a plant, the tissues are formed in various ways with respect to cell shape, thickness and arrangement of cell wall layers, orientation of the cellulose microfibrils as well as chemical composition. The basic assembly of plant cell wall structure are nanometer thick semi-crystalline cellulose fibrils embedded in amorphous matrix polymers. Our objective is to characterize this nanocomposite, in order to gain better insights into optimization strategies of living plants as well as into the material design as such.

For this purpose we investigate the structure-function-relationships of plants at the micro- and nanoscale by carrying out microtensile tests combined with X-ray scattering, Raman spectroscopy, FT-IR microscopy and Environmental Scanning Electron microscopy.

Molecular Deformation Mechanisms

A) Slip-Stick Mechanism

Molecular deformation mechanisms of wet wood were studied by straining tissues and single fibres in a tensile stage monitoring stress response and collecting XRD signal using a two-dimensional (2D) CCD detector. Experiments were carried out at the ESRF Grenoble (European Synchrotron Radiation Facility). By relating stress-strain curves and XRD results, it was shown that the microfibril angle (MFA) of the cellulose fibrils significantly decreased with the applied strain.

In addition, further cyclic micro-tensile tests combined with video extensometry were performed in order to obtain stress-strain relations for individual cells and tissue foils in laboratory conditions.

At small deformations up to a yield point, a steep slope indicates a stiff material. Beyond the yield point, permanent deformation occurs without serious damage to the material since after releasing the stress, the original stiffness is recovered. The mechanical behaviour of individual cells is essentially the same as for intact tissue, except that intact tissue usually breaks at smaller strains. During cyclic loading, the stiff response at small stresses is always preserved in the region beyond the yield point **(Fig. 1)**.

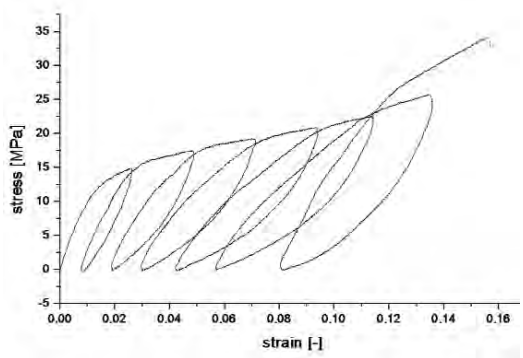

Fig. 1: Stress-strain diagram of wet compression wood tissue of spruce (MFA ~45°) in cyclic loading

Although, the structure of wood has nothing in common with that of metal the stress-strain behaviour of wood with high MFAs (e.g. compression wood) shows several characteristics that would normally be considered as typical for metals. The key properties of metals for their success as structural materials are their stiffness coupled to a reasonable plastic deformability, provided by the gliding of dislocations in the crystalline matrix.

The polymer assembly of the plant cell wall does not allow for a movement of dislocations. In our simple model for the deformation process, a large number of hydrogen bonds are able to transmit shear stresses between cellulose fibrils. When a certain shear stress is exceeded, the unspecific bonds break and there is a viscous flow of the matrix beyond the yield point. As soon as the stress is released, there is no back-flowing but a lock-in at the new position and the hydrogen bonds can reform immediately in the new position of the fibrils **(Fig. 2)**.

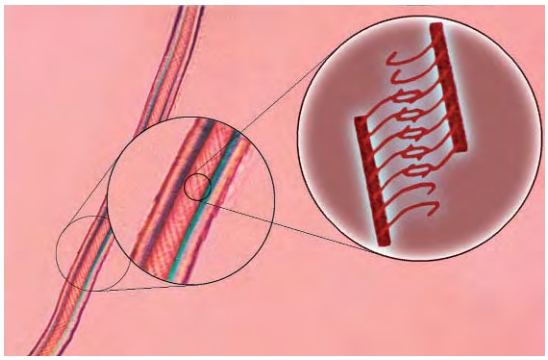

Fig. 2: Single compression wood tracheid in polarized light and schematic drawing of the "Velcro-connection" between the cellulose fibrils.

The plant biomaterial shows permanent plastic deformation without significant mechanical damage of the matrix, such as those usually observed in metals. The gliding of dislocations in metals, is replaced by a molecular stick-slip mechanism operated by some sort of "velcro" connection.

B) In-situ Raman Spectroscopy

A microtensile testing device was developed to strain thin plant tissue sheets and acquiring Raman spectra simultaneously. By relating stress-strain curves and changes in the Raman spectra, it is possible to evaluate molecular deformation mechanism as a function of external strain and strain rate. In a preliminary study 40 µm thick tangential sections of earlywood of pine were tested **(Fig. 3)**.

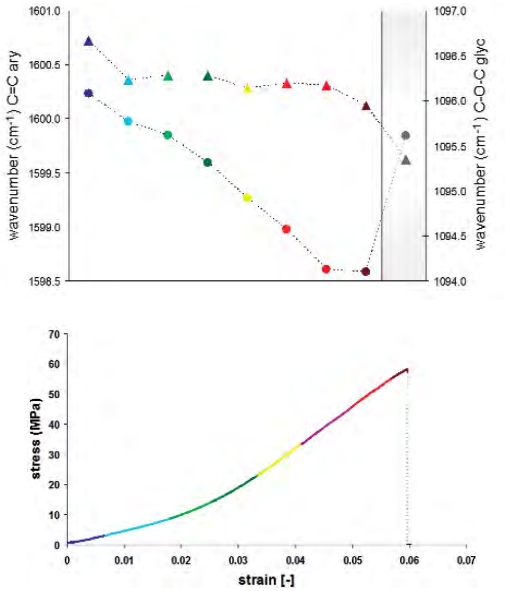

Fig. 3: Wavenumber shifts of C-O-C glyc (cellulose) and C=C aryl (lignin) at different stages of the tensile experiment. Curves and points are coloured according to the phases of tensile deformation in the stress-strain diagram (grey shadow = sample broken)

Spectra acquired during deformation show changes in peak intensity, peak shape and peak position. For instance, the band at 1095 cm^{-1} (C-O-C, glyc) corresponding to the stretching of cellulose is shifted progressively towards shorter wavenumbers **(Fig. 3)**, a demonstration that the cellulose molecule in these wood fibres are subjected to a uniform stress deformation. Almost no shift occurred for the 1600 cm^{-1} band corresponding to the amorphous lignin, which indicates although the lignin might be deformed, it is non-load bearing. Future in-situ tests will be applied to wood tissues with varying microfibril angle and polymer composition and will give new insights into deformation mechanism at the molecular level.

Specific Modification of Plant Cell Wall

A) Secondary Cell Wall Modification

The mechanical performance of plant cell walls is based on the mechanical properties of the individual components and their interaction according to the polymer assembly. Consequently, the mechanical relevance of a cell wall component depends decisively on its spatial orientation and bonding characteristics.

The basic idea of this project was to suppress the functioning of individual polymers in the mature cell wall of secondary xylem cells. Single fibres were isolated mechanically and the cell wall assembly was modified using specific enzymes. Micromechanical tests on the modified material were carried out to characterize its mechanical behavior without the missing component and thus, to learn more about the mechanical relevance of the eliminated polymer. Preliminary microtensile tests revealed the mechanical relevance of the eliminated polymers. Further enzyme treatments will target various hemicelluloses with the long term goal of developing a cell wall model based on the mechanical polymer interactions.

B) Primary Cell Wall Modification

A recent complementary approach to the foregoing project is to investigate structure-function relationships of primary plant cell wall components at the molecular level. In conjunction with the MPI for Molecular Plant Physiology (Lab. M. Pauly) we draw synergisms from the unique combination of plant physiology/enzymology/genetic engineering on one hand and micromechanical/ultrastructural characterization on the other. Harvested Arabidopsis hypocotyls are treated with various wall polysaccharide hydrolyzing enzymes to suppress the mechanical function of specific cell wall polymers. In a second approach hypocotyls are grown under the influence of the various enzymes. Micromechanical tests on the natural and on the modified hypocotyls from both approaches reveal the mechanical influence of the individual components, the interrelation of the polymer assembly, and potential compensation strategies of the plant.

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Biotemplating

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Aims

Plant tissues can be used as scaffolds or moulds to design novel nanostructured inorganic materials. The challenge is to preserve or to replicate the entire hierarchical structure of the original tissues from macroscopic down to molecular length scales. Our actual research concentrates on the relationship between the local microstructure and mechanical properties of carbon materials from organic precursors, such as carbon fibres or monolithic carbon from wood and other plant tissues. An important question from a fundamental as well as from a practical viewpoint is, whether the cellulose microfibrillar orientation in the original plant cell walls can be transformed into a preferred orientation of the resulting carbon template. Other recent interests in our group relate to silica in plants with the prospects of direct synthesis of biomorphous SiC materials, and to nanocasting of wood by nanoparticle infiltration in order to synthesize novel functional ceramics.

Results

Carbon Fibers

Modern carbon fibres are based on polymeric- (polyacrylnitrile, PAN) or pitch-based precursors, and exhibit extremely high values of tensile strength and Young's modulus up to very high temperatures, making them superior low-weight materials for countless high-tech structural applications. However, the detailed microstructure and its development during the application of high loads as required for technical applications are still largely unknown. We have intensively investigated the local microstructure and its relation to mechanical properties in single carbon fibres by applying position resolved and in-situ diffraction techniques based on synchrotron radiation **[1,2]**. In a recent experiment **[3]** we combined in-situ bending of single carbon fibres with highest position resolution by scanning diffractometry across the bent fibres using a 100 nm sized X-ray beam provided by a waveguide structure. This experiment, performed at the microfocus beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, provided microstructural parameters such as the microstrain and the orientation of the carbon sheets depending on the local macroscopic strain in the compression and the tension zone of the bent fibre. As a major result, it was found that the neutral zone was shifted with respect to the centre of the fibre, which can be understood by a difference of the elastic modulus in compression and in tension. This difference can be explained by different orientation distributions of the carbon sheets under a specific loading pattern. In particular, strong buckling of the sheets in the compression regime could clearly be identified experimentally for some pitch-based fibres as compared to PAN-based fibres, indicating fundamental differences in the cross-linking of the sheets within the two fibre types. Further exploring the important role of these cross-links and to understand their physical origin is one of the future challenges of our work.

Wood Pyrolysis

Wood pyrolysis, i.e., the non-oxidative conversion of wood into charcoal has been extensively investigated from a chemical point of view, but not much is known about the structural development and the mechanical properties of the carbonaceous residue. Such knowledge is essential, however, if the material is used as a template for advanced composites based on the hierarchical structure of wood. We have therefore studied the structural development of the carbonaceous residue by combined small- and wide-angle X-ray scattering **[4]** and the local mechanical properties at the level of single cell walls by nanoindentation, both as a function of pyrolysis temperature T up to 2400°C. At least 5 regions with distinct differences in microstructural appearance and mechanical response can be distinguished (**Fig. 1**): i) degradation of the biopolymers and a decrease of the elastic modulus E to a very low value; ii) a fully disintegrated, amorphous structure at constant E; iii) formation and lateral growth of aromatic carbonaceous layer stacks as well as development of nanoporosity accompanied with a strong increase of E; iv) further lateral growth of carbon sheets at constant E; 3D growth of carbon "crystallites" and decreasing E. In particular, a preferred orientation of the carbon sheets parallel to the original wood cell axis develops with increasing T, indicating that the original cellulose molecular orientation might have been preserved.

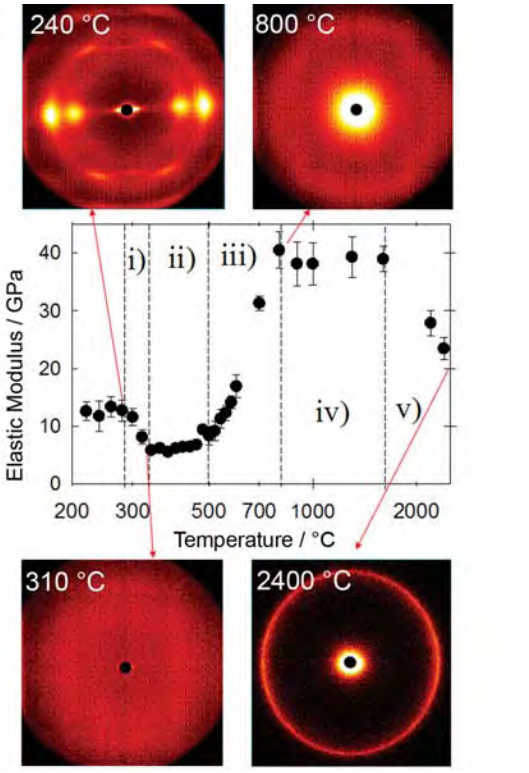

Fig. 1: 2D X-ray scattering patterns from pyrolysed spruce wood sections (cell axis vertical, range of d-spacings 0.25 nm - 6 nm), together with the temperature development of the reduced elastic modulus of the cell wall material.

The decrease of the modulus at high temperatures might be a consequence of this preferred orientation, since cell cross-sections were indented. However, the ultimate origin of the preferred carbon orientation, the mechanical response in terms of microstructure and chemical bonding, as well as the whole thermal conversion process are still to be explored in more detail.

Besides the carbonaceous residue as a biomorphous material, we are also interested in the details of the thermal degradation process of the biopolymers at the first stages of pyrolysis. To this end we have built a special heating device for in-situ X-ray scattering and have performed in-situ measurements of the kinetics of cellulose degradation up to temperatures of 400°C at the synchrotron radiation source HASYLAB (beamline A2) in Hamburg. The data of this recent experiment are currently still being evaluated.

Other Projects

Some annual plants contain considerable amounts of Si, mostly in the form of silica (up to 10 wt %), whose origin and biological function is still a matter of debate across several disciplines. Besides the potential use as a cheap and renewable source for direct SiC synthesis, the silica skeleton might be used as a scaffold for the synthesis of biomorphous ceramics. First studies on horsetail stalks (equisetum hyemale) show indeed that the ash of carefully calcined specimens replicates largely the original plant structure. Current work focuses on the detailed distribution of silica (see **Fig. 2**) as well as on its microstructural and chemical appearance.

Fig. 2: X-ray microCT reconstruction of a horsetail stalk (diameter of the stalk ≈ 3.5 mm). Red overlays are regions of particularly high X-ray absorption, indicating strong silica accumulations.

Another project that just started deals with the prospect of nanocasting plant cell walls by nanoparticle infiltration. The aim here is to copy the detailed cellulose microfibril orientation into a ceramic material. First synthesis approaches with CeO_2 nanoparticles have been undertaken, but no definitive positive templating results can be reported to date.

Two further projects which do not directly concentrate on biotemplating but rather on biomimetic/biomechanical aspects have recently been initiated. First attempts were undertaken to map the chitin orientation in the neighbourhood of mechanoreceptors in insect cuticles using scanning microbeam X-ray diffraction. The particular aim here is to understand the role of local fibre orientation on the function of integral strain sensors. Together with the "plant research group" in the Department of Biomaterials we furthermore started recently to explore the structure directing role and the dynamics of water in the nanopores of wood cell walls. In this context, a research proposal has been submitted within the Collaborative Research Center (SFB) 448 "Mesoscopically Organized Composites".

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Biomimetic Materials

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Monika Rumpler (since October 2004)
Alexander Wöß (since October 2003)
Inderchand Manjubala (since February 2004)

The general aim of this group is to use knowledge of the building principles of natural hierarchical composites, such as bone **[1,2]** and wood **[3]** to improve existing materials just by shaping and structuring. While chemical composition and supra-molecular structure are well-known to determine the material properties, biological systems demonstrate that mechanical and other properties can also be modulated in a wide range just by an appropriate geometrical arrangement of the material in space. Examples are spiralling fibre structures with varying spiral angle, as in the wood cell for example **[3]**, or the architecture of the cancellous bone in the interior of a vertebra **[2]**. One of the goals was to explore this paradigm, assuming that it should be possible to "tune" the mechanical properties of various porous materials (ceramics, polymers or composites) by controlling the pore architecture. A second goal was to develop porous scaffolds with controlled pore geometry for bone cell culturing. Most of this work was carried out in collaboration with the University of Technology and the Ludwig Boltzmann Institute of Osteology, both in Vienna, Austria.

Rapid Prototyping (RP)

In order to structure porous materials in the micron to millimetre range, rapid prototyping technology was established in the Department. The potentials of two different systems were explored, one based on photolithography and a second one based on inkjet printing. In both cases, three-dimensional structures are built layer by layer from a model constructed on a computer. The first process is shown schematically in **Fig. 1**: a layer of photosensitive resin is selectively exposed to visible light and polymerised. Three-dimensional structures are built by moving the building platform continuously upwards.

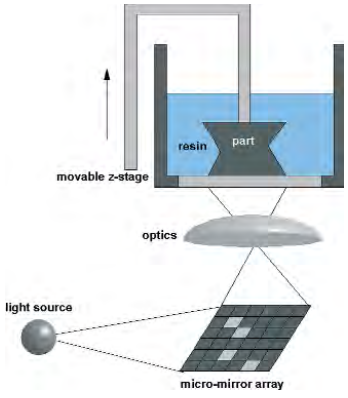

Fig. 1: The principle of rapid prototyping based on photolithography.

The second rapid prototyping process corresponds to a wax printer as sketched in **Fig. 2**. Three-dimensional structures are built by writing successive layers using two types of waxes, the (blue) building wax and the (red) support wax, which is later removed by a solvent. Both techniques allow free-form fabrication of arbitrary structures with a pixel resolution in the range of 30 microns.

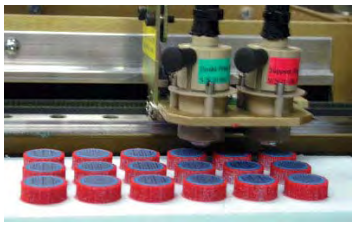

Fig. 2: Porous structures being built by inkjet printing using two types of waxes.

Mechanical Properties of Cellular Solids with Controlled Architecture

A number of porous structures with different internal architecture have been designed on the computer and built with rapid prototyping **(Fig. 3)**.

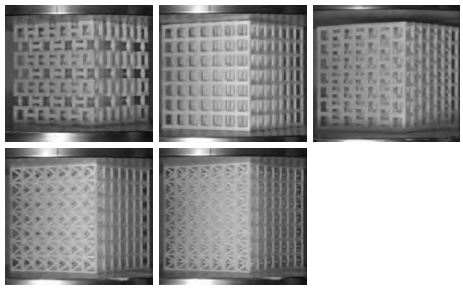

Fig. 3: Cellular Solids with constant apparent density, but varying architecture.

The idea was to test the influence of the internal geometry on the mechanical properties. Cubic specimens were designed with a given overall size, shape and apparent density, but with different internal architecture. The mechanical properties, such as stiffness or impact energy absorption efficiency, were observed to vary within at least a factor three **[4]**. This project is being continued by studying the orientation dependence of the properties, as well as the influence of special types of defects. Moreover, the performance of artificially designed structures will be compared to structures reconstructed from natural models such as cancellous bone using same resin as for the artificial structures.

Bioceramic Bone Replacement Materials

Using the RP equipment mentioned above, we produced casting moulds for cellular bone replacement materials. Using RP methods offers the possibility to produce almost arbitrary geometries, which can be beneficial not only from a mechanical point of view, but also from a biological point of view, as the cell ingrowth behaviour strongly depends on the geometry of the porosity of an implant. To produce ceramic structures with continuous pores with a diameter in the range of 500 microns, a polymer casting mould was first constructed by RP. The structure chosen is sketched in **Fig. 4** and corresponds to a "woodpile arrangement" with layers of parallel struts. The struts in two successive layers were oriented 90° to each other. In this structure, the hollow space has the same geometry as the filled space.

Fig. 4: woodpile structure as designed

This structure, covered with a mantle, was produced in resin as a casting mould for ceramic gel casting: Ceramic powder (we mostly used commercially available hydroxylapatite (HA) powder) was mixed with water, monomers and a polymerization initiator. Vacuum was used to fill the mould with the ceramic slurry. Polymerization occurred during a following thermal treatment, giving the cast part some strength. Further elevation of the temperature caused the water to evaporate, then the mould to burn off and, finally, led to sintering of the ceramic particles. Typical structures obtained by this process **[5]** can be seen in **Fig. 5**.

Fig. 5: resin casting moulds (red) and hydroxyapatite structures obtained by RP and ceramic gel casting

Bioceramic/Biopolymer Composite Bone Replacement Materials

In bone material, organic fibres (collagen) and mineral nanoparticles are combined at the nanometre scale. To mimic this situation, porous scaffolds were also made of a composite of the biopolymer chitosan with apatite particles. Chitosan has been used before as a matrix for three-dimensional tissue growth and is a potential candidate for tissue engineering and drug delivery systems. The composite scaffolds were produced by RP using dissolvable wax moulds. This was necessary since temperature treatment (to remove resin scaffolds produced by other RP techniques) was not possible due to the chitosan component in the scaffolds. The scaffolds were then freeze-dried and cross-linked to produce micro pores in addition to the macropores **(Fig. 6)**.

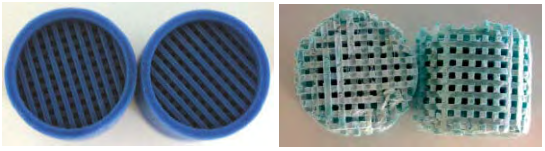

Fig. 6: wax moulds (left) and chitosan/HA composite scaffolds (right).

Biocompatibility of Bone Scaffolds:

The fabricated hydroxylapatite and chitosan/apatite scaffolds were assessed for their biocompatibility with bone cells using a pre-osteoblastic cell line, known to be able to differentiate into active osteoblasts. Cells were covering the scaffolds, sometimes in several cell layers, and they produced extra-cellular matrix in 3 weeks **[5]**, as seen from histological staining **(Fig. 7)**.

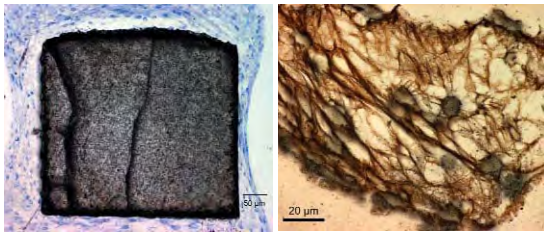

Fig. 7: Histological sections of the ceramic scaffolds after a culture period of 14 days. Giemsa staining shows cells covering the whole surface of a strut (left), Gömery staining reveals the formation of an extracellular matrix consisting of collagen (right).

Nanoparticles

Some activity was started to control the size and shape of hydroxylapatite (HA) nanoparticles by precipitation reactions involving use of specific ligands which can affect the nucleation and growth mechanism in addition to reaction parameters like precursors, solvent system, temperature and pH. The rationale is that the specific shape of the HA nanoparticles and their interaction with the organic component plays an important role in the mechanical properties of the biominerals. Additionally controlling the size and shape of the HA nanoparticles, their functionalisation and self-assembly to get materials with hierarchical structures is also interesting for various applications including bone implants, catalyst supports and radioactive waste management.

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Synchrotron Beamline at BESSY

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Thesis: Structure and Properties
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Since 2003: Group Leader
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Aims

Hierarchically structured (bio)materials are a central research topic in the Department. Such materials need to be characterized by a variety of methods and over many length scales. This cannot be achieved by conventional methods of structural analysis and requires further development of experimental techniques, for example, scanning small-angle (SAXS) and wide-angle X-ray scattering (WAXS), and corresponding data analysis methods **[1-5]**. Currently, we are developing a scientific instrument at the microfocus beamline at BESSY II in Berlin Adlershof, with the main goal to implement a scanning device for the combination of simultaneous SAXS, WAXS and X-ray fluorescence analysis (XRF). This unique combination of methods will allow to map structural parameters from the atomic/molecular to the nanometer level as well as chemical composition with a spatial resolution given by the beam size of a few micrometers. Since our long-term goal is to proceed from microbeam scanning to a real imaging technique, a major task is the development of sophisticated software tools for interactive instrument control combined with online data analysis, which is done in cooperation with partners from the European Synchrotron Radiation Facility (ESRF). For the preparation of biological specimens and the development of specimen platforms such as cryo-cooling techniques, a sample preparation laboratory is also under construction.

Beamline and Experimental Station Development

The microfocus beamline at BESSY is a joint project between the Max Planck Society, BESSY GmbH, and the Bundesanstalt für Materialforschung (BAM). The measuring station is developed in close collaboration with these partners and with the Technical University Berlin. The beamline was built by an external company (ACCEL) and has been installed in December 2004 as a second branch of the 7 T wavelength-shifter of the BAMLine at BESSY II. The final beamline commissioning is scheduled for April 2005. For the SAXS/WAXS/XRF experimental station, five fixed energies (4-24 keV) from a combined Bragg-Fresnel - bimorph mirror system with a beam divergence < 1 mrad, a beam size ≤ 5 µm and a photon flux $\geq 10^9$ ph/s will be available. The principal design of the station **(Fig. 1)** was developed during 2004, and the main components have been purchased.

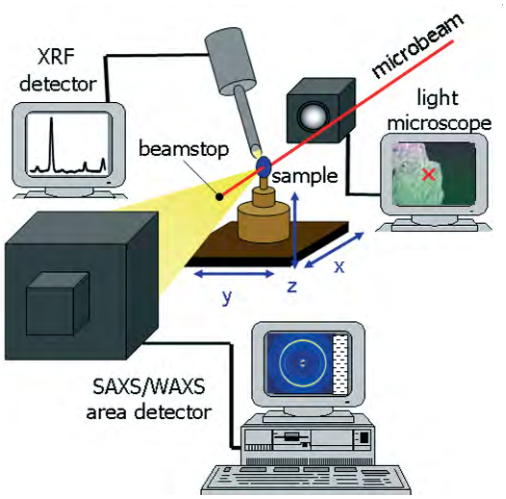

Fig. 1: Schematic layout of the SAXS/WAXS/XRF experimental station at BESSY

Cornerstones of the experimental setup are a flexible and modular goniometer with a high precision scanning stage (0.2 µm resolution), a high-resolution, on-axis optical microscope, and a high-resolution, large-area CCD detector with fibre-optic taper (MarMosaic). Using this detector with the given small size and divergence of the beam, up to three orders of magnitude in the length of the scattering vector q can be covered simultaneously, and thus, SAXS/WAXS with a single detector and a resolution down to $q = 0.1$ nm^{-1} will be feasible ($q=4\pi/\lambda\sin(\theta)$, where 2θ is the scattering angle and λ is the wavelength). The installation of the experimental station is scheduled for April 2005 and first test experiments can be anticipated for Summer 2005.

Online Data Analysis

Scanning SAXS/WAXS experiments produce 2D scattering patterns as a function of (at least) two scanning coordinates. This results typically in many thousands of 2D patterns, and consequently, data reduction and analysis needs to be at least partially automated. Moreover, it is highly desirable to get an overview of the progress of an experiment (e.g., to decide about follow-up measuring strategies), and therefore, the experimental setup should allow for a online mapping of some selected simple parameters deduced from the scattering patterns. In the long-term, online mapping of microstructural and chemical parameters derived from SAXS/WAXS/XRF data by pre-defined automated data reduction and -evaluation procedures should bring the technique eventually to a similar level as current scanning electron- or scanning probe microscopy techniques.

In the framework of a long-term project at the ESRF (2004-2006, LT-proposal SC-1579), three European laboratories from MPI-Golm, ESRF-Grenoble, and CITER-Cardiff have constituted a research consortium on "Scanning X-ray diffraction of hierarchical biological tissues". An important common goal of the consortium is to develop a software platform for interactive instrument control and online data-reduction and -analysis. The actual version of the package consists of a PYTHON-based "toolkit" developed by M. Burghammer (ESRF), interfacing with the instrument and with sophisticated data analysis programs such as FIT2D. In the future, this package will be continuously improved by the partners and will be implemented at the experimental station at BESSY.

A preliminary version of the software was successfully tested during the first beamtime of the LT-proposal in November 2005. Several biological materials such as osteonal bone, insect cuticle or eggshell were investigated, and "simple" parameters derived from the 2D patterns such as the total scattered intensity were mapped online. **Fig. 2** shows an example of osteonal bone, where the total SAXS intensity clearly reflects the lamellar structure of the osteon.

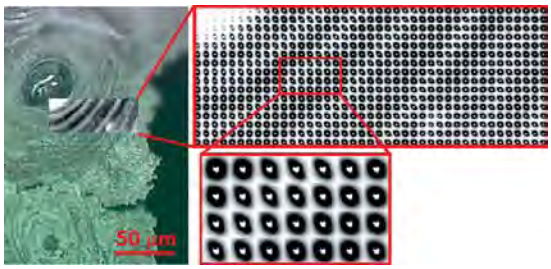

Fig. 2: Image of the integrated SAXS intensity (insert), and of the 2D SAXS patterns from osteonal bone (data taken at ESRF, beamline ID13 with 1 µm beam size from a Kirkpatrick- Baez mirror system).

Closer inspection of the shape of the SAXS patterns shows that the contrast is actually an orientation contrast, arising from an alternating orientation of the mineral platelets with respect to the osteon axis.

Bio Preparation Laboratory

Investigation of soft matter using synchrotron radiation requires adequate sample preparation which is as important as the measuring process itself. The structure of highly hydrated samples such as biological tissues or single cells is strongly altered by dehydration procedures. Moreover, radiation damage due to the high brilliance of synchrotron radiation is one of the most critical issues for biological systems. Therefore, special preparation procedures and measurements under cryo-cooled conditions are frequently necessary, which emphasizes the need for a properly equipped laboratory in the direct neighbourhood of the beamline. A particularly important task is the development of proper sample platforms which allow the transfer of (cryo-cooled) specimens between different instruments, such as the SAXS/WAXS/XRF station, optical microscopes, infrared- or Raman spectrometers, etc.

The planned bio-preparation laboratory in its first construction phase will comprise equipment for conventional cryo-preparation procedures such as freeze drying and critical point drying, and a cryo-microtome to prepare thin sections of tissues. The Lab is presently being built and equipped in a concerted action between our group, BESSY and the University of Heidelberg and should be ready to work in the second half of 2005.

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References:

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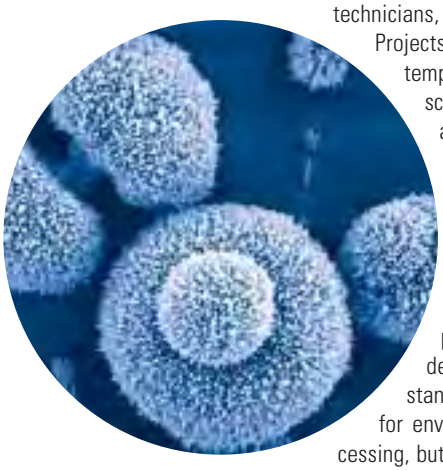
COLLOID CHEMISTRY

Research in the Department of Colloid Chemistry



Scientific Profile

The activities of the Colloid Chemistry Department are a mixture of "old" strongholds found in the former Institute, activities brought by the director, and new topics developed by young researchers. The overall size of the department is 60 people, covering a wide range of research topics.

The effective constituting elements of the group are "projects", a structure headed by senior scientists involving technicians, graduate students and post-docs (3-8 people). Projects are related to scientists, but usually have a temporal character of ca. 5 years. Then, permanent scientists (including the director) have to reevaluate their profile. In the case of non-permanent scientists, the projects usually leave the department with the promotion of the scientist to the new academic environment without competition of the institute.

Incentives for the choice of a new research direction are usually scientific curiosity and promise, but research is also driven by the demands of industry and society. The strong standing of heterophase polymerization as the base for environmentally friendly coatings and plastic processing, but also the development of better analytical tools are typical examples where stimuli came from the outside. In detail, the following topics are treated by the department:

- Heterophase Polymerization
- Self-organizing Polymers
- Mesoporous Materials & Nanoparticles
- Modern Techniques of Colloid Analysis

Heterophase Polymerization

"Heterophase Polymerization" summarizes the techniques of suspension-, emulsion-, mini-, and microemulsion-polymerization. The solvent is usually water, but heterophase polymerization in organic media is also examined. This class of techniques, although 90 years old, experiences a strong renaissance, since it allows the production of high polymer containing formulations in water as an environment-friendly solvent. Solvent free coatings and glues are just two examples where polymer dispersions are present in daily life.

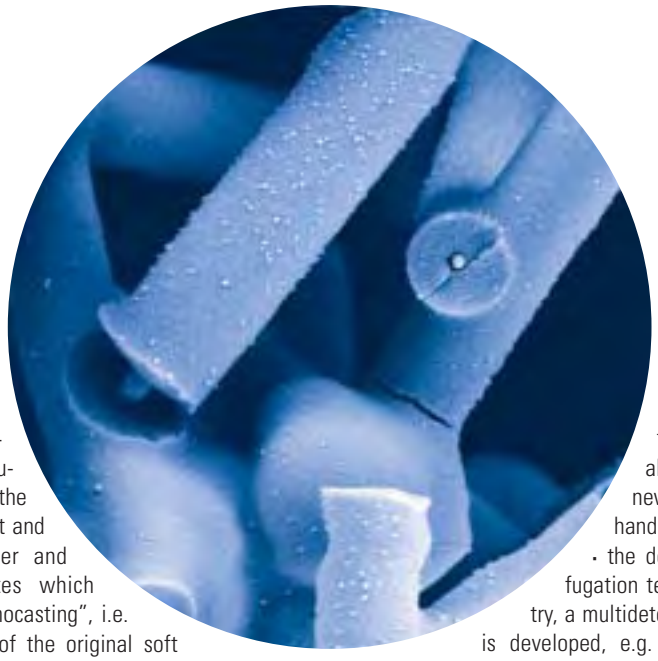
Central points of interest of the project teams working on heterophase polymerization are:

- to gain a better understanding of the nucleation period and particle formation. For this purpose, new experimental online multidetection techniques are developed and supplemented by theoretical approaches (Dr. Klaus Tauer).
- to simplify the synthesis of complex polymer molecules (e.g. block & graft copolymers) and colloids (e.g. core-shell latices, reinforced materials) by emulsion polymerization and rational use of the particle interfaces (Dr. Klaus Tauer).
- Inisurfs, Transsurfs, and Surfmers, and new stabilizers for better polymer dispersions (Dr. Klaus Tauer).

Self-organizing Polymers

Amphiphilic polymers consist of components with different solubility, e.g. a hydrophilic and a hydrophobic part. Both components can be sensitively adjusted to the dispersion medium as well as the dispersant, and "extreme" dispersion problems can be solved. Focal points of interest in this range are:

- The micelle formation and lyotropic liquid crystalline phase behavior of amphiphilic polymers is examined in dependence of molecular parameters as well as the amount of solubilized material (Dr. Helmut Schlaad).
- The introduction of secondary interactions such as H-bridges, dipole interactions or metal-ligand binding results in superstructures with more complex order (Dr. Helmut Schlaad).
- The performance of molecular drugs can be highly enhanced by coupling to a colloidal system with synergistic action. The specific knowledge on functional polymers and colloids is used in cooperation with pharmaceutical/ medical partners to generate tailor made colloidal drug carriers and diagnostics (Dr. Helmut Schlaad).
- Amphiphilic polymers can step in the precipitation of inorganic and organic matter and control the growth of the particle by biomimetic or polymer-controlled mineralization. So-called double-hydrophilic block copolymers where one block mediates water solubility and the other interacts with the surface of the particles are examined and enable the design of drugs, fillers and pigments and of new reinforced materials (Dr. Helmut Cölfen).
- In biochemistry, complex molecules (proteins and RNA-strands) are made on a technical level by reliable and reproducible automated procedures. The transfer of this technology to polymer and colloid science and its application to non-natural monomers and coupling reactions allows the synthesis of single species polymers (without polydispersity) with specific functionality in the milligram and gram scale. This technology is used to generate blockwise conjugates between peptide and synthetic polymers blocks. Minority peptide blocks are expected to "ordinate" the otherwise disordered synthetic block. We also expect that such polymers help to address the interface between the biological and technical world (Dr. Hans Börner).



Mesoporous Materials & Nanoparticles

Template routes have recently been extended to surfactant assemblies. Our contribution in this field is the use of more robust and adjustable polymer and colloidal templates which allows a real "nanocasting", i.e. a 1:1 replication of the original soft matter template into an inorganic nanostructured replica. Current activities in this field include:

- the employment of membranes and beads as supports for designer catalysts where nanoparticle formation is an integer part of the nanostructure set-up and profitably controlled by either the porogens or the pore geometry (Dr. Markus Niederberger, the "Zeit-Project" together with the Fritz Haber Institute).
- the synthesis of new well defined nanoparticles with function by solvent and ligand assisted synthetic pathways and their self-assembly into organized 3D superstructures by ligand encoding (Dr. Markus Niederberger)
- the use of nanocasting as an analytical tool, i.e. to characterize fragile soft matter superstructures, such as the worm-like assemblies of cyclodextrines or other supramolecular entities (Markus Antonietti)
- implementation of experiments within the pore system for "nanochemistry, i.e. the analysis of specific effects of a nanoconfinement on a physical properties and chemical reactions (Markus Antonietti)
- the generation of crystalline thin mesoporous layers by evaporation induced self-assembly (EISA) for catalysis, electrochemistry and sensing (Dr. Bernd Smarsly)

Modern Techniques of Colloid Analysis

All the work described above is necessarily accompanied by a considerable amount of colloid analysis. This includes fully commercial techniques, but also implies the development of new techniques or methods of data handling, as:

- the development of new ultracentrifugation techniques. Together with industry, a multidetection kit for the ultracentrifuge is developed, e.g. coupling the separation with Raman-, UV- or fluorescence detection. This allows an in-situ chemical analysis within a separating complex colloidal mixture and revitalizes the AUC. (Dr. Helmut Cölfen together with the BASF AG). New gradient techniques for the AUC such as pH-, chirality- or enzymatic activity gradients reveal new information about complex spatio-temporal phenomena (Dr. Helmut Cölfen).
- special techniques of transmission and scanning electron microscopy on soft, structured matter (Dr. Jürgen Hartmann).
- the improvement of diverse techniques of hydrodynamic chromatography such as thermal field flow fractionation and asymmetric flow field flow fractionation (Dr. Helmut Cölfen)
- computational analysis of high precision static light scattering experiments (Dr. Gudrun Rother)
- development of new techniques of dynamic light scattering to colloidal systems, e.g. using optical near fields or the "ellipsometric light scattering" (Dr. Reinhard Sigel).

Larger Equipment and Central Service Labs of the Department

Commercial standard techniques which are available in the department are: Transmission and scanning electron microscopy, static and dynamic light scattering, diverse techniques of light microscopy, various chromatographic facilities, reaction calorimetry with online multidetection, analytical and preparative ultracentrifugation, thermal analysis, DSC, porosimetry, and FT-ATIR for liquid analysis.

One laboratory, the electron microscopy lab, is a so-called "central service lab", i.e. it belongs and is operated by the department, but is designated to perform scientific routine measurements for the whole institute.

Markus Antonietti,
Director of the
Department
of Colloid
Chemistry

Heterophase Polymerizations – Polymer Dispersions

Klaus Tauer 27.09.1951
1974: Diploma, Polymer Chemistry (Friedrich Schiller University, Jena) Thesis: On the photoconductivity of polyarylene-vinylene polymers
1978: PhD, Polymer Chemistry (Friedrich Schiller University, Jena) Thesis: Investigations of spectral sensitization of photoconductivity of polyarylene-vinylene polymers
1977-1991: Scientific Coworker (Institute for Polymer Chemistry, Academy of Sciences, Teltow)
1987: Habilitation, Chemistry (Academy of Sciences, Teltow) Thesis: Modelling emulsion polymerization of vinyl chlorid
Since 1992: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Controlled Radical Polymerization in Aqueous Heterophase Polymerization (S. Nozari)

The field of controlled radical polymerization has been, and continues to be, one that carries strong interest from both the academic and industrial polymer communities. Among the various techniques to tame free radical polymerizations the reversible addition fragmentation chain transfer (RAFT) process is one of the most recent developments, since only 6-7 years, but one of the more efficient methods in this field regarding versatility and robustness. In a comprehensive experimental study the possibilities of controlling *ab-initio* aqueous heterophase polymerizations via the RAFT process with hydrophobic dithioester transfer agents were investigated. Special emphasis was placed on the interplay between the hydrophilicity/hydrophobicity of both the RAFT agents and the primary initiator radicals.

Fig. 1

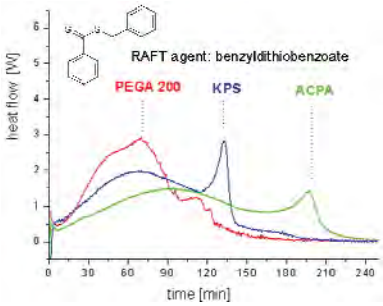
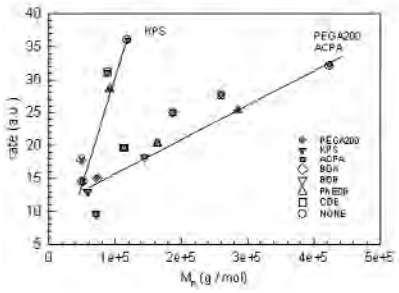


Fig. 2



Conditions

Recipe:
80 g of water, 4 g of 5% aqueous SDS solution, 20 g of Styrene, $4.26 \cdot 10^{-4}$ mole of RAFT agent, $3.41 \cdot 10^{-4}$ mole of initiator, T = 80 °C, reaction calorimeter CPA200, in all runs complete conversion

The selected data in **Figs. 1** and **2** confirm that in RAFT aqueous heterophase polymerizations the achievable average molecular weight and the average rate of polymerization can be tailored by the proper choice of both the initiator and the RAFT agent **[1]**. Among the RAFT agents investigated benzyldithioacetate leads to the highest degree of control as expressed by the lowest polydispersity index of the molecular weight distribution with 1.5 compared with 4 for the uncontrolled polymerization.

Interfacial Energy Promotes Aqueous Heterophase Polymerization (N. Öz, DD. He, S. Nozari)

It was found **[2]** that aqueous heterophase polymerization can be carried out at room temperature without redox-systems if the surfactant concentration is above the critical micelle concentration and the initiator concentration is greater than 6 mM **(Fig. 3)**. This effect was observed for different initiators regardless they are water- or oil-soluble and various types of surfactants (anionic, cationic, nonionic, monomeric, and polymeric).

Fig. 3

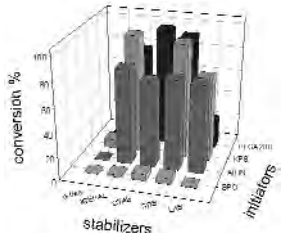
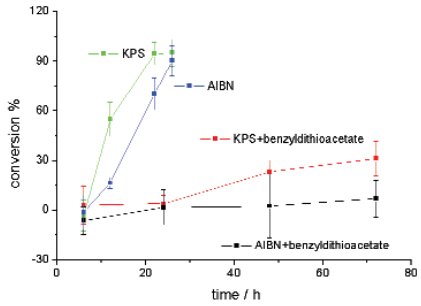


Fig. 4



Conditions

Recipes:

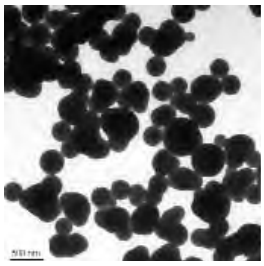
Fig. 3: 25 °C, 36 hours, rotation thermostat, 10 g of water, 0.1 g of stabilizer, 0.67 ml of styrene, 60 mg of initiator, (e-free : stabilizer-free)

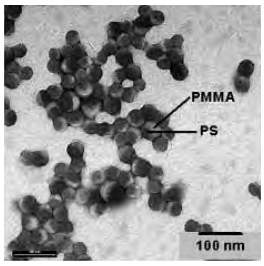
Fig. 4: as for Fig. 3 but 0.02 g of AIBN, 0.033 g of KPS, 0.028 g of benzyldithiobenzoate RAFT agent

Compared with elevated temperatures the rate of polymerization is drastically reduced. Hence, it was possible to detect differences between oil- and water-soluble initiators especially during the initial period which have not been seen hitherto **[2]**. In the presence of RAFT agents **(Fig. 4)** the polymerization is even more slowed down thus proving the maintained activity of the RAFT agent.

Synthesis of Model Colloids (A. M. I. Ali, N. Shirshova, M. Mukhamedjanova)

This project focuses on the preparation of various types of model colloids such as special double hydrophilic block copolymer particles as exemplary poly(diethylaminoethyl methacrylate)-b-poly(N-isopropylacrylamide)-b-poly(methacrylic acid cross-linked) (PDEAEMA-PNIPAM-PMAA) **[3]**, monodisperse latexes in the size range between 100 and 2000 nm, and the exploration of possibilities to get composite particles with diameters much less than 100 nm preferentially below 50 nm. Exemplary, the double hydrophilic particles can be used as stabilizers in aqueous hetero-phase polymerizations leading to a special particle shape due to limited flocculation (TEM image **Fig. 5**).





Conditions

Recipes:

Fig. 5: 50 g of water; 5 g of styrene; 0.025 g AIBN; 0.04 g of PDEAEMA-PNIPAM-PMAA stabilizer particles; 50 °C

Fig. 6: seed: 15g of styrene, 0.785g of DPE, 1g of surfactant E30, 2.1g of KPS, 250g of water, composite: seed swollen with MMA and AIBN for 24 h; 70 °C; stained with $CsOH/RuO_4$

The attempts to synthesize composite particles as small as possible is illustrated by the TEM picture of polystyrene-*b*-poly(methyl methacrylate) particles **(Fig. 6)** made from polystyrene-1,1-diphenylethylene (DPE) precursor particles by the so-called DPE method **[4]**. The block copolymer yield is almost 100 % as no homo-poly(methyl methacrylate) has been detected.

Particle Nucleation in Aqueous Heterophase Polymerizations (S. Kozempel)

The investigations were concentrated on the elucidation of the so-called "Jumbo effect" meaning an increase in the transmission during the particle nucleation period as described in **[5]**. Results of multi angle laser light scattering investigations as described in **[6]** questioned the generally accepted assumption that a styrene in water solution (without macroscopic phase separation) consists of only molecularly dissolved molecules. Contrary, these measurements revealed that a saturated styrene solution in water contains also droplets with average diameters of about 300 nm. During the equilibration period both the size and the number of drops increases. This saturation of styrene with water lasts up to several hours depending on temperature and stirrer speed. Basically, the MALLS data have been confirmed by UV spectroscopy (red squares in **Fig. 7**) and gas chromatography (not shown here).

The black squares in **Fig. 7** prove the enormous influence of the degree of saturation of the continuous water phase with the styrene monomer on the duration of the pre-nucleation period. Its duration varies almost by a factor of ten i.e. between 40 and 4 min at the lowest and highest degree of saturation, respectively. Moreover, the intensity and the duration of the Jumbo effect are influenced by the monomer concentration in the aqueous phase before starting the polymerization. The greater this concentration is the less pronounced the increase of the transmission during the nucleation period.

Fig. 7

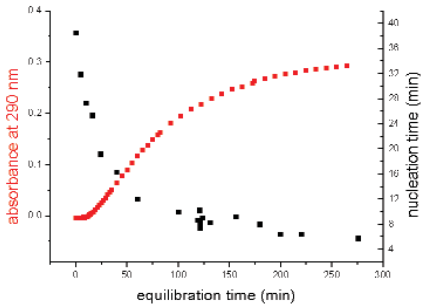
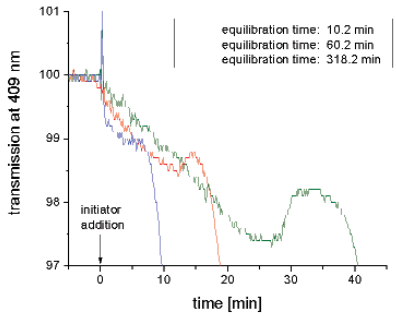


Fig. 8



Conditions

Recipe:

Figs. 7, 8: 390 ml of degassed water, 3.3 g of styrene, 10m of 20 mM KPS solution, 70 °C

UV data in Figs. 7 and 8 monitored with Uvikon 931 at 290 nm and Spekol 11 at 409 nm, respectively

Hence, the Jumbo effect might be caused by an increased monomer flux from the droplets through the water phase into the particles leading to a decrease in the index of refraction between the continuous phase and the scattering objects as, compared with pure water, the index of refraction of the continuous phase and of the particles is increased and decreased, respectively, due to the higher styrene concentration.

Co-operation

The MALLS-investigations during the particle nucleation period of aqueous heterophase polymerization were carried out in collaboration with G. Rother from the "Colloid Chemistry" department. Special double hydrophilic triblock copolymer particles and diblock copolymers were applied in crystallization processes in collaboration with the "Biomineralization" group (H. Coelfen). Thermo-sensitive block copolymers and colloidal particles with N-isopropylacrylamide blocks were prepared for investigations in the "Thin Liquid Films" group of the "Interface" department (R. von Klitzing). Monodisperse polymer particles in the size range between 300 nm and 1.2 µm were prepared and supplied for various investigations in the Heyrovsky Institute Prague (Marketa Zukalova), the ETH Zurich (Vahid Sandoghar), and the University Leipzig (Friedrich Kremer).

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Biomimetic Mineralization

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1993: PhD, Chemistry (University of Duisburg)
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1993-1995: Postdoc (National Centre for Macromolecular Hydrodynamics, University of Nottingham)
Since 1995: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
2001: Habilitation, Chemistry (University of Potsdam)
Thesis: Biomimetic mineralisation using hydrophilic copolymers: Synthesis of hybrid colloids with complex form and pathways towards their analysis in solution

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In this project, the polymer controlled crystallization of inorganic and organic compounds is investigated as a mimic of natural biomineralization processes **[1]**, **[2]**, **[3]**. The goal is to apply model systems in order to understand the basic processes and self assembly mechanisms to complex hierarchically structured materials **[4]**. Whereas we have initially focused on the preparation of complex crystal morphologies by polymer controlled crystallization, we have started to analyze selected systems in detail in the report period to elucidate the structure formation mechanisms supported by computer modeling using the Cerius^2 software. Synchroton small angle X-ray scattering (SAXS) with high time resolution for the system $CaCO_3$ revealed that the applied double hydrophilic block copolymers (DHBC's) act as initially proposed: One part interacts with the crystal surface of a nanoparticle directly after its formation and sticks to it, whereas the other part provides an at least temporary stabilization, so that aggregation of amorphous primary nanoparticles is delayed but not suppressed **[5]**. These nanoparticle building units aggregate and crystallize and lateron form spherical vaterite superstructures.

Small angle neutron scattering (SANS) was also applied to understand the formation of spherical $CaCO_3$ superstructures via rod and dumbbell precursor morphologies under control of a Poly(ethylene oxide)-block-Poly(methacrylic acid) DHBC **[6]**, **[7]**, **[8]**. Time resolved contrast variation experiments revealed that the polymer concentration is low but homogeneous inside the crystalline superstructures throughout the rod-dumbbell-sphere morphogenesis process, whereas the inorganic structure continuously densifies from a loose aggregate to a compact structure as evidenced from the power law behaviour. In addition, the block copolymer yields smaller primary particles, which initially are amorphous and surprisingly, the majority of the polymer remains in solution and does not participate in the crystallization process.

Parallel to these mechanistic investigations, we continued our synthetic efforts to understand the formation of complex crystal morphologies by self assembly of nanocrystal precursor particles. For example, a template as simple as a CO_2 gas bubble can be used to generate complex flower-like, shuttlecock and hollow half sphere self-assembled $CaCO_3$ morphologies from polymer stabilized nanoparticle precursors via variation of the solution surface tension **[9]**. Another open question in polymer controlled crystallization is if the secondary polymer structure of dissolved macromolecules plays an important role as suggested from the two dimensional templates in nacre biomineralization. We therefore synthesized peptide DHBC's, where the secondary structure could be reversibly switched from random coil to a-helix via pH or temperature changes and applied these additives for $CaCO_3$ crystallization **[10]**. Against the expectation, the highest level of control over the crystallization process could be achieved with the random coil conformation. This speaks against the epitaxial match between mineral and polymer, as suggested in biomineralization. Instead, a high density of functional groups on the mineral surface seems to be of more importance than an unflexible polymer template.

However, if a stiff molecule is applied, which selectively matches a crystal surface, a highly selective adsorption to this face can be achieved resulting in complete inhibition of this face from further growth. This is demonstrated for the (111) face of gold, which can be stabilized by a hexacyclen DHBC resulting in very thin crystalline gold platelets, which are transparent in the electron beam and show interference patterns upon bending (see **Fig. 1**) **[11]**.

Fig.1: Left: 1,4,7,10,13,16-Hexaazacyclooctadecan (Hexacyclen) macrocycle adsorbed on gold (111) Right: TEM micrograph of gold platelets with exposed (111)

A mineral system, which forms very complex self-repetitive hierarchical structures by polyacrylate triggered oriented attachment of $BaSO_4$ or $BaCrO_4$ nanoparticles to fiber bundles or cones is shown in the figure below **[12]**. These structures are very similar to those, previously obtained in presence of phosphonated block copolymers but have more defects in the bundle structure as a result of the worse nanoparticle stabilization capability of polyacrylate.

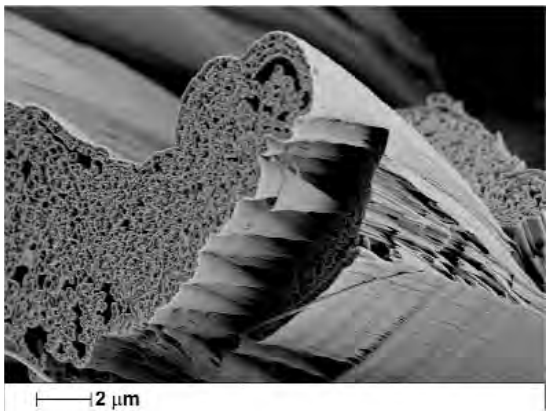


Fig. 2: Hierarchical $BaSO_4$ superstructures by oriented attachment and self assembly of $BaSO_4$ nanoparticles triggered by polyacrylate.

It was possible to generate single fibers by attachment of particles to the fiber surface as steric blockers upon fiber growth resulting in very high aspect ratio single crystalline $BaCrO_4$ nanofibers **[13]**. Simultaneous application of a DHBC, which generates $BaSO_4$ fibers and one, which generates $BaSO_4$ spheres resulted in a cumulative growth mechanism at low polymer concentrations e.g. fibers growing on spheres (see **Fig. 3**) **[14]**.

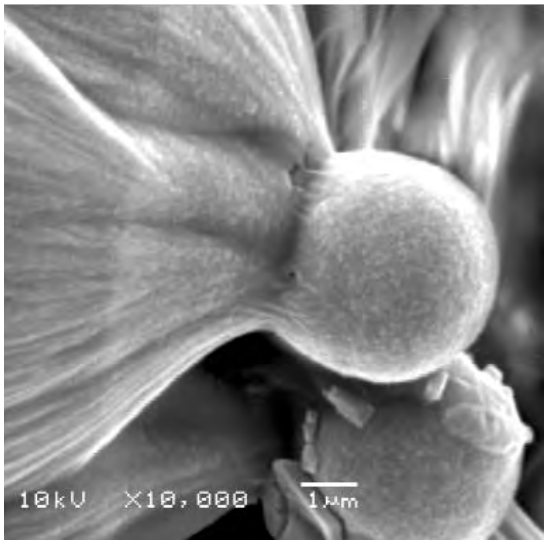


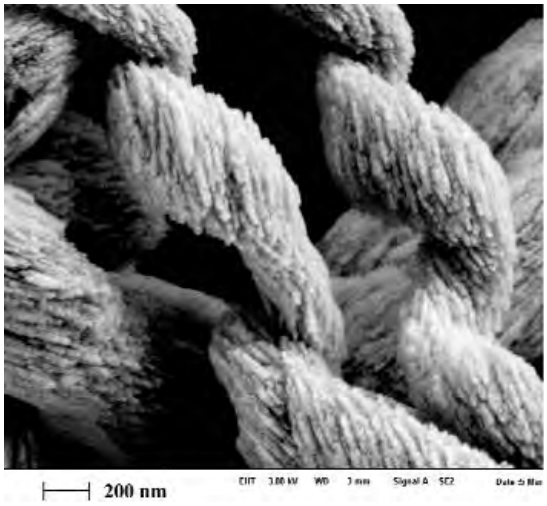
Fig.3: $BaSO_4$ fibers growing on first formed spheres demonstrating additive effects of the structure directing DHBC's in a mixture.

However, at higher polymer concentrations, the action of the DHBCs is cooperative resulting in new morphologies, which are no derivatives of the underlying spheres or fibers anymore.

Reduction of silver salts in presence of starch under hydrothermal conditions yielded silver fibers coated with carbon, which were very uniform in diameter indicating that a polymer can fulfill multiple roles in a controlled crystallization process **[15]**.

Other investigated polymer controlled crystallizing systems were self assembled $BaCO_3$ spheres and dumbbells **[16]** and $CaCO_3$ hollow sphere formation via a sacrificial spherical template of metastable vaterite **[2]**. Also, we have explored the stabilization capability of DHBC's for the generation of high quality CeO_2 nanocrystals **[17]**, ways to control morphologies of various cerium compounds via solvent variations **[18]** and a procedure to generate ternary interpolymer complexes with silica **[19]**.

Our approach enabling selective adsorption of block copolymers to code defined crystal surfaces and to trigger the self assembly to complex morphologies could even be applied to generate chiral helical nanocrystal superstructures from a racemic phosphonated polymer and achiral $BaCO_3$ (see **Fig. 4**) **[20]**.



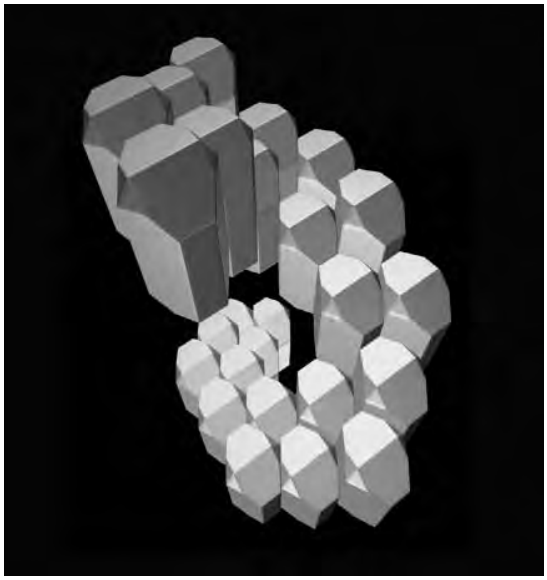


Fig. 4: Upper: Self assembled $BaCO_3$ helices generated by selective coding of orthorhombic nanoparticle faces with a phosphonated stiff polymer. Lower: Schematic representation of the nanoparticle self assembly to a helix

Here, the steric demand of a block copolymer leads to a staggered arrangement resp. axial growth with a direction defined by the first three aggregated nanoparticles. On the other hand, a clockwise or counterclockwise turn is preferred by the requirement of epitaxial matching of a further attaching nanoparticle to the existing aggregate. Overlay of these two processes leads to the observed helix formation. These processes show the level of control, which can be achieved by polymeric additives.

H. Cölfen, H. Endo, N. Gehrke, P. Kasparova, Y. Luo, N. Nassif, M. Page, M. Riedl, J. Rudloff, T. X. Wang, S. Wohlrab, A. W. Xu, S. H. Yu
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Functional Mesostructured Inorganic-Organic Materials – Advanced X-ray Scattering Methods

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Materials composed of self-assembled nanoscaled domains, such as mesoporous structures, are of crucial importance for various future technologies such as catalysis, photovoltaics and smart devices. Our research is directed towards the fabrication of nanostructures of classical materials like carbon and also metal oxide species with functionality such as electrochroism, etc., for instance in the form of thin coatings. Mesostructured metal oxides (e.g. TiO_2) can be obtained through sol-gel templating using suitable templates as structure-directing agents: the metal oxide is formed by sol-gel reactions within the hydrophilic domains of a lyotropic mesophase, obtained from the self-assembly of amphiphiles in water or other polar solvents. The underlying strategy is to develop and use suitable templates, possessing optimum self-assembly properties, because structural perfection of these materials is not accessible through standard templates. The self-assembly and the solidification of these mesoscopic systems are studied by novel experimental and theoretical concepts of x-ray scattering, which are also applied to a profound characterization of mesostructured materials.

Ionic Liquids as Templating Reagents

In the past years, growing interest emerged in ionic liquids (ILs) as reaction media and solvents in chemical processes. In addition, we observed that certain ionic liquids can also serve as excellent templates for the generation of mesostructured materials such as mesoporous oxides and nanoparticles. In this project, the special templating properties of ILs are explored in detail and used for the fabrication of previously inaccessible materials. For instance, a hierarchical porous material could be made using colloidal particles, a block copolymer ("KLE", $(H(CH_2CH_2CH_2(CH)CH_2CH_3)_{89}$ $(OCH_2CH_2)_{79}OH)$ and an IL as templates, leading to porous silica with the small pores being organized with the walls of the corresponding larger pores **[1]** on three length-scales. While the block copolymer produces spherical mesopores of ca. 14 nm, the IL gives rise to 3 nm mesopores, both pore types located in the walls of macropores (350 nm) of tuneable size. The hierarchical pore arrangement is clearly seen in Transmission Electron microscopy (TEM) and small-angle x-ray scattering (SAXS) data, revealing a dense mutual packing of the KLE mesopores and the IL mesopores between them, providing an extremely high porosity. Surprisingly, the ordering of the KLE mesopores is not disturbed by the presence of the IL. These results suggest different, superior templating behaviour of ILs compared to standard surfactants **[2]**.

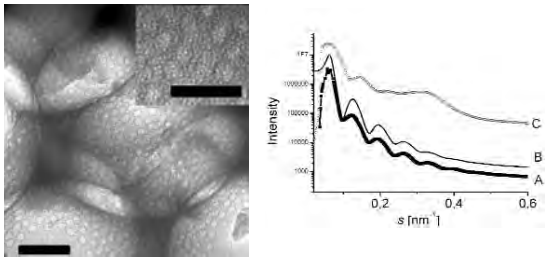

Fig. 1: TEM images (left) of a trimodal porous silica. The scale bars correspond to 100 nm and 50 nm. Right: SAXS patterns. A: Mesoporous silica (KLE). B: Simulation of A. C: Trimodal porous silica.

Fabrication and Characterization of Thin Films of Mesoporous Metal Oxides with Crystalline Pore Walls

Sol-gel chemistry in combination with a suitable structure-directing amphiphile is a versatile strategy for the fabrication of mesoporous films of crystalline metal oxides. Typically, after dip-coating of a solution containing a metal precursor (alkoxides, etc.) and a template, a suitable temperature program is necessary to generate the crystalline mesoporous oxide nanocrystals in the pore walls. However, the fabrication of such materials usually involves difficulties due to mesostructural collapse, and several oxides had not been reported at all in this form. The KLE templates significantly facilitated the fabrication of crystalline mesoporous binary and ternary oxide films **[1-3]**. For the first time chemically pure, highly crystalline mesoporous CeO_2, HfO_2, MoO_3, WO_3, Fe_3O_4, Ta_2O_5 and perovskites were obtained, allowing for a detailed understanding of the particularity of these templates compared to standard amphiphiles. The main research objective is the elucidation of the self-assembly and crystallization mechanism, and also the study of physico-chemical properties, such as electrochroism for WO_3, as a function of the porosity and pore size. The crystallisation and mesostructural changes upon temperature (T) treatment were studied by T-dependent SAXS and WAXS, High-Resolution TEM, Atomic Force Microscopy (AFM) and physisorption, as exemplified for CeO_2 mesoporous films **(Fig. 2, 3)**. Together with AFM and TEM **(Fig. 2)**, from a novel quantitative SAXS analysis **(Fig. 3b)** the size and aspect ratio of the deformed spherical pores could be determined for the first time with high precision, e.g. 6 nm normal and 14 nm parallel to the substrate in this case. The walls consist of cerium oxide nanoparticles, which grow upon temperature treatment **(Fig. 3a)**, but not exceeding the wall thickness imposed by the block copolymer.

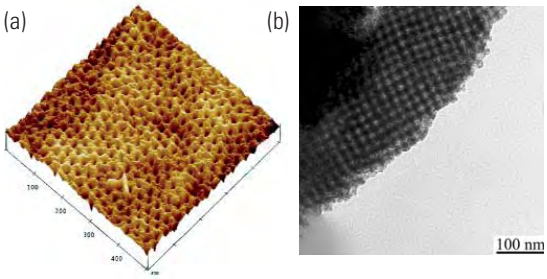

Fig. 2: AFM (a) and TEM (b) images of a mesoporous CeO_2 film with crystalline pore walls.

Our studies revealed that key features of these polymers are an enhanced thermal stability and hydrophilic-hydrophobic contrast **[1-3]**.

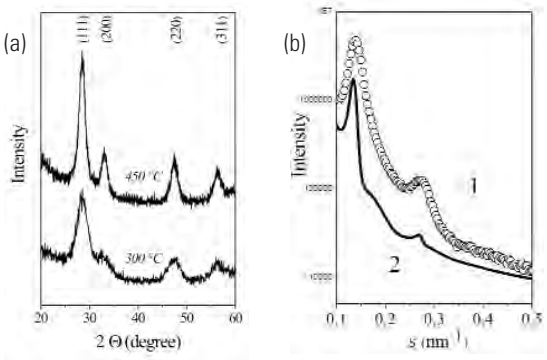

Fig. 3: CeO_2 mesoporous films: WAXS as a function of temperature (a) and SAXS (b) 1: experimental 1D SAXS data, 2: fitting based on ref. [5]).

Also, the block lengths are designed to be long enough to allow for sufficiently thick walls, being compatible with the growth of nanoparticles without destroying the mesostructure.

Structural Characterization of Carbons by X-ray Scattering Methods

Porous carbons have been used for hundreds of years and represent an important class of porous materials. In spite of their widespread application

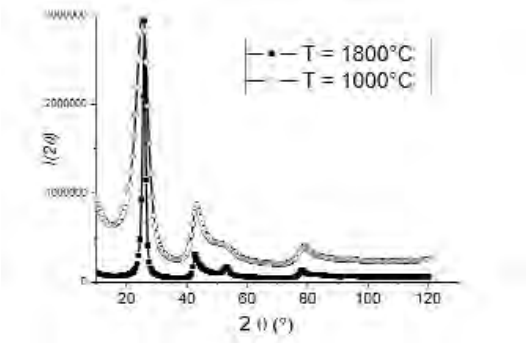

Fig. 4: WAXS analysis [6] of two carbons, treated at different temperatures.

(e.g. in filtering etc.) the details of their microstructure are still unclear, in particular the relationship with macroscopic properties (sorption). In this project mesostructures of carbons are produced and studied by the combination of novel WAXS/SAXS evaluation techniques which are developed and compared with Raman spectroscopy and physisorption. **Fig. 4** shows the successful fitting of entire WAXS curves of carbons for the first time by a novel approach **[6]**, providing various structural parameters.

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Nanostructured Materials by Ionic Self-Assembly: Function and Switchability

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The use of the ionic self-assembly strategy and a basic understanding of the property-structure-function relationship **[1]** has been established for the production of nanostructured materials. Building on the initial work with azobenzene dye-surfactant complexes, the use of single-crystal Xray analysis has provided further insights into unexpected packing motives found for such complexes (see **Fig. 1** below). **[2]**

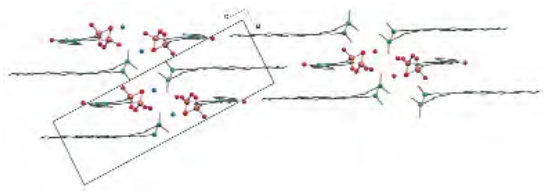

Fig. 1: The triclinic unit cell of a dye-surfactant complex. Note that no π stacking is found.

However, to investigate and expand the possibilities to incorporate further functionalities and interaction motives into such nanostructured materials, several approaches were used. These included the following, which will be briefly discussed below:

Complexes with Perylenediimide Dyes:
The orientation of liquid-crystalline materials into large monodomain structures are of importance for applications in display devices and as optical components.

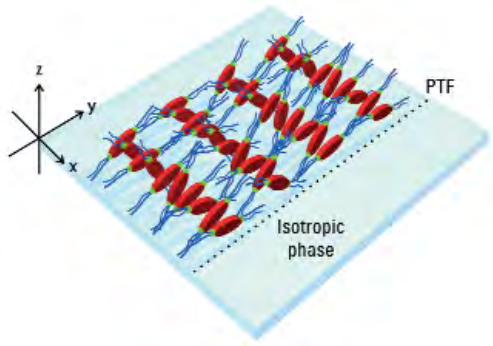

Fig. 2: Orientation of the perylenediimide tectons at the phase transition front (PTF).

We have found that, by making use of branched double-tail surfactants, it is possible to produce lyotropic perylendiimide-surfactant complexes. **[3]** Although all conventional methods for orientation of such lyotropic phases (in DMSO) failed, it was found that a phase-transition front (PTF) developed during an isotropic-lyotropic phase transition. This led to the formation of highly oriented large monodomains of the perylene dyes with a dichroic ratio of close to 20. Null-ellipsometry confirmed the 3D orientation of the perylendiimide tectons, as depicted in **Fig. 2**.

In a bid to exploit the use of this versatile tecton, a cationic perylenediimide derivate and an oppositely charged phthalocyanine dye were combined in a 1:1 charge ratio. **[4]** Combination of the two tectons leads to the formation of highly viscous organogels. These gels were investigated by a number of techniques, indicating that very long polymeric fibers of stacked dye molecules were formed.

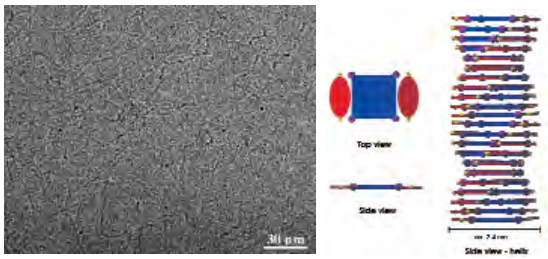

Fig. 3: Cryo-TEM micrograph showing the presence of infinitely long fibers (left). Schematic representation of the helical stacking motive found (right).

Digital analyses, in conjunction with AFM, TEM and X-ray analyses, indicated that the dyes interact to form side-by-side stacked helical polymeric aggregates.

Liquid-Crystalline Material from Discotic Precursors
The use of discotic precursors for the formation of columnar LC phases is well known. The use of further intermolecular hydrogen bonding has been used to stabilise such phases, and even cause gelation behaviour at low concentration.

The combination of hydrogen bonding and the ISA synthesis route was used to investigate the possibilities to mimic the covalent routes presented before. Synthesis of a charged tricarboxyimide derivative and subsequent complexation with surfactants led to the formation of columnar LC phases. **[5]** In one specific case gelation behaviour was observed at very low concentrations in DMSO and DMF.

Continuing investigations into the use of hetero-atom-containing discotic precursors led to the use of tricycloquinazoline (TCQ) core as tecton. **[6]** Hydrolysis of a hexaalkoxy precursor led to the in-situ formation of a hexa-anionic tecton. Complexation of this potential discotic core with double tail surfactants yielded, surprisingly, a lamellar LC phase **(Fig. 4)**.

Further investigations **[7]** using small multicharged discotic tectons, such as benzene hexacarboxylicacid (BHC), led to similar results as found for the TCQ core. After complexation with double tail surfactants, X-ray analyses (both transmission and reflection mode), null-ellipsometry and temperature-dependent UV and IR analyses proved the existence of very large monodomains of spontaneously aligning Smectic A phases, with the layers aligned parallel to the substrate surface.

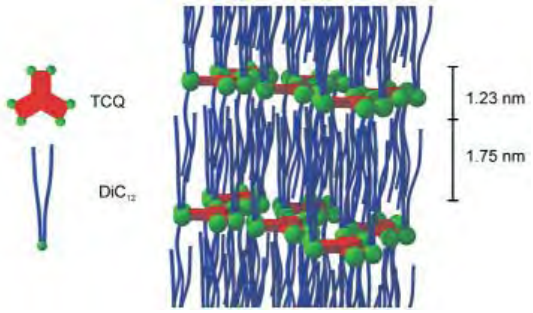

Fig. 4: Schematic representation of the packing of the TCQ tectons into a lamellar phase structure.

Functional ISA Complexes – Towards Devices

In a bid to explore a variety of different materials for use in ISA complexes, a new class of highly luminescent polyoxometalates were synthesized and complexed with both normal alkyl as well as ferrocene-derived surfactants. **[8]** The influence of the phase and packing behaviour and the presence of electron-accepting moieties were investigated by a variety of techniques, including determinations of lifetimes and absolute quantum yields. A lyotropic LC phase was described for the first time for polyoxometalate complexes **(Fig. 5)**.

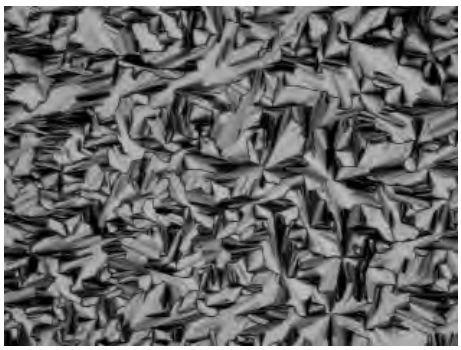

Fig. 5: Lyotropic POM-surfactant phase in chloroform.

In a continuation of the project investigating reactions within confined environments, a ternary co-polyaddition of a unsaturated surfactant, dithiol and diene was employed. **[9]** This led to the incorporation of varying amounts of polymerised materials into lamellar phase structures.

However, the incorporation of a polymerisable surfactant does not ensure the presence of functionality within an ISA complex. Investigations have therefore turned toward the production of pyrrole-containing surfactant systems for the production of conducting nanostructured materials. These surfactants were synthesized, and their thermotropic and lyotropic phase behaviour studied in detail. **[10]**

In a separate investigation into the use of conducting tectons, well-defined phenyl-capped tetra- and octaaniline materials were synthesized. **[11]** These materials were then used for the formation of soft, nanostructured ISA complexes. Temperature-dependent investigations indicated the existence of reverisble structural transitions at higher temperatures. This was confirmed by conductivity measurements, which showed highly reversible 3 orders of magnitude changes in the conductivity of the tetraaniline complexes.

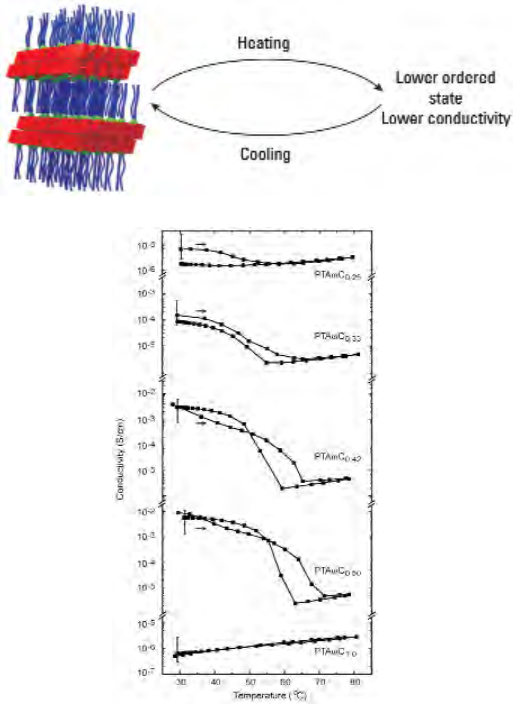

Fig. 6: Switchable conductivity in TANI-surfactant complexes.

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Bioorganic-Synthetic Hybrid Polymers as Molecular LEGO® -Bricks

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Introduction

Controlled processes of structure formation, yielding defined, hierarchical structures, are one of the most important tools in biological systems to realize well-adapted, high-performance materials (e.g. bone, mussel shells, hair and wool etc.).

Particularly polypeptides and proteins provide beautiful examples of highly controlled structure formation processes. Precisely defined structures are essentially needed for the complex function of such molecules (e.g. mussel byssus thread, spider silk, aqua- or ion-porins, enzymes, etc.).

We have contributed our efforts to transfer native structure formation principles observed in polypeptide systems towards the organization of synthetic polymers. This biomimetic approach might advent new possibilities in the design of structured polymeric materials **(Fig. 1)**.

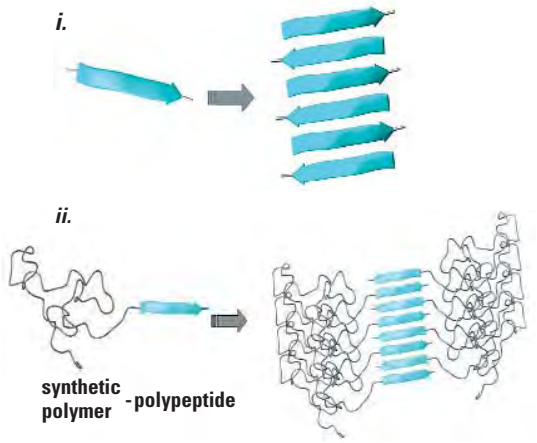

Fig. 1: Schematic presentation of the organization of synthetic polymers induced by oligopeptides;
(i) Organization of beta strands into a β-sheet motif;
(ii) Induction of structure in hybrid building blocks via self-assembly of oligopeptide-based organizer units.

Aims and Strategy

- Design of building blocks by conjugation of oligopeptide-based organizer units to synthetic polymers (e.g. poly(ethylene oxide), poly(meth)-acrylates, polystyrene, etc.)
- Investigation of structure formation via spontaneous or induced self-assembly of the building blocks.
- Understanding of the relationship between chemical structure of the organizer unit and resulting organization of the building blocks.
- Rational design of defined structures in polymeric materials by tailor-made organizer units.

Synthetic Approaches

To access polymer-organizer building blocks (e.g. AB-block copolymers, **Fig. 1, *ii***) routes have to be developed allowing the defined conjugation of synthetic polymers to oligopeptides. Difficulties during conjugation often originate from the multifunctional character of the oligopeptides as well as from different solubilities of oligopeptide and polymer.

Two major synthetic strategies were investigated:

i. Polymerization approaches include the sequence specific introduction of an initiator functionality to an oligopeptide. The resulting macroinitiator is applied in a controlled radical polymerization process to initiate the polymerization of synthetic monomers (e.g. *n*-butylacrylate). Defined polymer-oligopeptide conjugates could be obtained exhibiting controllable molecular weight and low polydispersity **(Fig. 2)**. **[1]**

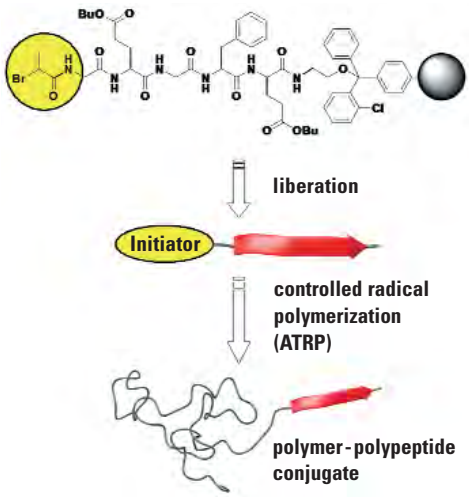

Fig. 2: Schematic presentation of the oligopeptide macroinitiator approach.

ii. Coupling approaches that include the coupling of a synthetic polymer exhibiting a defined end-group functionality with a complementary, selectively addressable functionality of an oligopeptide. Contributions were made by developing routes to defined chain-end functionalities of synthetic polymers e.g. polyacrylates or polystyrene. Therefore controlled radical polymerization techniques were combined with either orthogonal protected functional initiators or highly specific chain-end-group transformation reactions. **[2]**

Pre-organized Oligopeptides as Organizer Units [3]

The attachment of oligopeptides to a suitable template results in the pre-organization of oligopeptide strands. The restriction in conformational freedom as well as optimization of the geometry of the strands increases mainly driven by entropy, the tendency to form aggregates. **[4]** Therefore pre-organized oligopeptides are potentially applicable as highly effective organizer units.

Derived from literature-known systems, a template was tailor-made to pre-organize two oligopeptide strands for the formation of an anti parallel β-sheet motif. The template design includes an additional functionality that can be selectively addressed to conjugate the synthetic polymer chain **(Fig. 3)**. As a proof of concept, poly(ethylene oxide) was conjugated as a first model polymer yielding water-soluble polymer-organizer building blocks. These allow the analysis of structure formation with established analytical tools in determination of protein structure e.g. UV-circular dichroism spectroscopy (UV-CD).

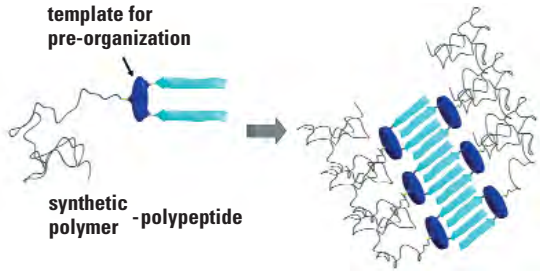

Fig. 3: Schematic presentation of the organization of synthetic polymers by template preorganized oligopeptides.

Consistent with the model in **Fig. 3**, strongly anisometric aggregates could be observed exhibiting a persistent stiff behavior **(Fig. 4)**. UV-CD spectroscopy verifies the presence of β-sheet secondary structures by exhibiting the typical Cotton effects (maximum at 195 nm and minimum at 218 nm) (**Fig. 4** inset).

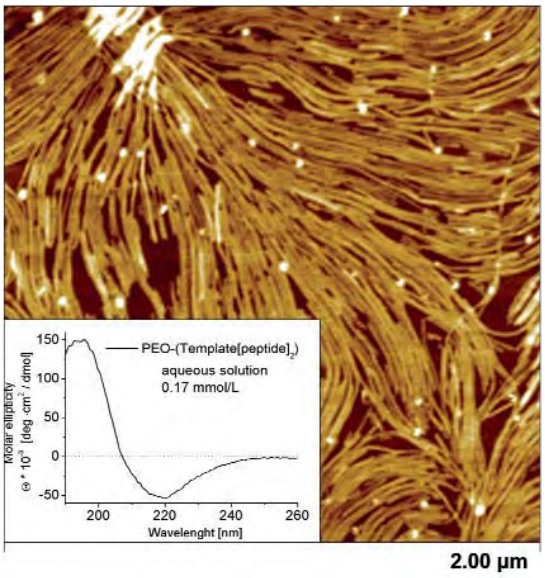

Fig. 4: AFM micrograph of anisometric aggregates of PEO-(Template-[Oligopeptide]$_2$); CD spectrum of the aqueous solution before spin coating (inset).

Biomedical Applications

The development of defined conjugates of synthetic polymers and oligo- or polypeptides allows the addressing of biomedical or pharmacological applications. Conjugates consisting of poly(ethylene oxide) and monodisperse polypeptides have been successfully applied as carriers for cytostatica in anticancer therapy. Contributions in this field were made by an improvement of the degree of definition of the applied carrier systems in comparison to existing carriers, by the development of a new application method of carrier drug conjugates as well as by the incorporation of "smart" features into the polymeric carriers e.g. predefined degradability.

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Amphiphilic Block Copolymers

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The research of the group is devoted to (i) the development of new controlled polymerization techniques and modular synthetic pathways, (ii) characterization of functional polymers, and (iii) study of the phase behavior of amphiphilic diblock copolymers. Particularly interesting are effects of secondary structures and specific interactions (electrostatic, dipole-dipole, hydrogen bridging interactions, etc.), which should add complexity to block copolymer mesostructures (biomimetics). The systems under study are "molecular chimeras" of synthetic polymers and α-helical polypeptides, polymers with chelating acetoacetoxy units, and complexes of copolymers with complementary recognition sites.

Block Copolymer Synthesis

Linear polypeptide-based block copolymers were synthesized *via* the ring-opening polymerization of α-amino acid *N*-carboxyanhydrides (NCA) initiated by ω-primary amino-functional polymers. Screening of the free amine initiating/propagating species as hydrochloride promoted a controlled polymerization of NCA **(Fig. 1)**, producing block copolymers with nearly monodisperse molecular weight distribution (MWD) (polydispersity index, PDI < 1.03) **[9, 14]**. Earlier reported recipes yielded polymers with PDI > 1.3.

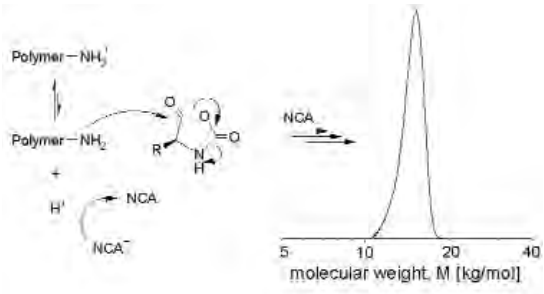

Fig. 1: Synthesis of polypeptide block copolymers by „ammonium-mediated" polymerization of NCA.

The radical addition of ω-functional mercaptanes to the vinyl double bonds of 1,2-polybutadiene-*block*-poly(ethylene oxide) was used for a modular synthesis of well-defined functional block copolymers **(Fig. 2)**. The modification reaction proceeds smoothly and yields quantitatively functionalized copolymer samples without altering the MWD of the parent polymer (PDI < 1.09) **[12]**.

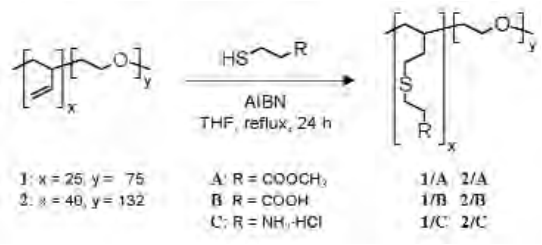

Fig. 2: Modular synthesis of functional block copolymers.

Block Copolymer Characterization

Absolute MWDs of diblock copolymers can be determined with conventional size exclusion chromatography (SEC) without referring to any kind of calibration curve and/or molar mass-sensitive detecting device. Evaluation of two independent detector signals provides the chemical composition, which together with the molecular weight of the first block segment (determined independently) yields the absolute molecular weight of every copolymer fraction. From this set of data, the MWD of the sample can be calculated. Results obtained by this method are in good agreement with the ones determined by NMR and SEC with on-line viscosity or multi-angle light scattering detection **[3]**.

Block Copolymer Mesostructures

Thick polymer films made from poly(Z-L-lysine)-polystyrene rod-coil block copolymers (PDI = 1.01-1.64) exhibit a hexagonal-in-zigzag lamellar morphology **(Fig. 3a)**. The zigzag superstructure results from the hexagonal packing of polypeptide helices being fractionated according to length. Thus, there is a correlation between the MWD of the polypeptide segment and the interface-curvature properties of the morphology **(Fig. 3b) [10]**.

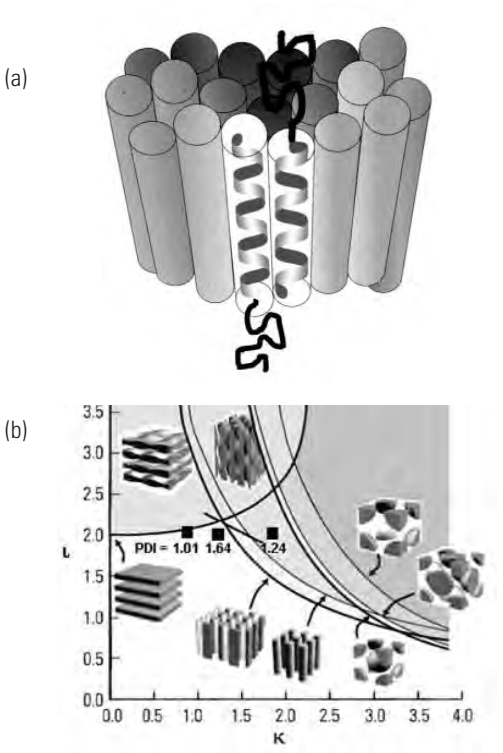

Fig. 3: a) Illustration of the undulated or zigzag lamellar structure of polypeptide block copolymers. b) Interface-curvature (ι-κ) properties of lamellar structures of polypeptide block copolymer with different PDI.

Poly[2-(acetoacetoxy)ethyl methacrylate]s can self-assemble into hierarchical superstructures, i.e. double-stranded helical tubes of either screw sense. Both diameter and pitch of the superhelices are ~12 nm and their length is 200-500 nm **(Fig. 4a)**. It is proposed that the polymer chains first organize into ribbons, the width of which determines the pitch of the helix, and then coil up into the helical superstructure **(Fig. 4b)**. Formation of these structures is driven by the establishment of hydrogen bridging interactions between adjacent acetoacetoxy groups and compensation of dipole moments **[13]**.

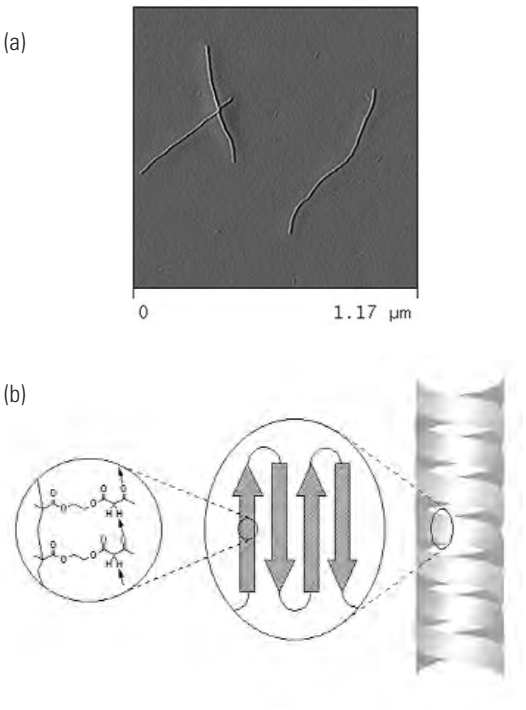

Fig. 4: a) Scanning force micrograph of poly[2-(acetoacetoxy)ethyl methacrylate] superhelices. b) Illustration of the hierarchical structure of superhelices.

Mixing of block copolymers with complementary recognition sites is used for the generation of a library of complex mesostructures **[2]**.

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Synthesis, Functionalization, Assembly and Application of Metal Oxide Nanoparticles

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Transition metal oxides constitute one of the most important classes of materials with properties covering almost all aspects of materials science and solid state physics such as semiconductivity, superconductivity, ferroelectricity, magnetism, and catalytic activity. Accordingly, they play an outstanding role in many emerging technologies such as sensing, pigmentation, catalysis, electroceramics, energy storage and conversion, and the trend towards further miniaturization of functional devices demands the production of nanoparticulate transition metal oxides with the highest possible purities, small crystallite sizes, well-defined particle morphologies, and small particle size distributions. It is expected that particle sizes in the nano-regime and specific crystal shapes enhance the performance, lower sintering temperatures, and allow a fine-tuning of the chemical and physical properties. However, the synthesis of nanoparticles is just the beginning towards their use in nanotechnology. In a next step, these nanoparticle building blocks have to be arranged into well-defined ensembles and superstructures leading to novel and unique properties that are not found in the individual components. One of the most promising strategies for the fabrication of such hierarchical structures is the use of self-assembly processes. The organisation is determined by the interactions among the primary building blocks, and there is no doubt that adequately tailored surface properties are the fundamental parameter in the design of novel nanobuilding blocks.

Our research goal is to develop general concepts for the fabrication of complex architectures, made up of nanocrystalline metal oxide components that are hierarchically ordered by specific interactions between the nanoparticle building blocks. We are focussing on three main objectives: i) synthesis of crystalline metal oxide nanoparticles with appropriate surface functionality, ii) assembly of these nanoscale building blocks into hierarchically organized superstructures, and iii) implementation of the gained expertise to fabricate nanodevices.

Nanoparticle Synthesis

In spite of the high scientific and technological interest in transition metal oxides, their synthesis at the nanoscale is still a big challenge and many complex metal oxides remain to be explored. In order to circumvent some drawbacks of aqueous sol-gel chemistry such as poor crystallinity, fast hydrolysis rate of transition metal alkoxides and presence of counter ions, we developed a variety of nonaqueous synthesis routes to transition metal oxide nanoparticles. The reaction of metal acetylacetonates, metal halides, or metal alkoxides with either alcohols, ketones, aldehydes or amines allows the preparation of a large collection of binary and ternary metal oxide nanoparticles such as TiO_2, V_2O_3, In_2O_3, Ga_2O_3, Nb_2O_5, Ta_2O_5, HfO_2, SnO_2, ZnO, $BaTiO_3$, $SrTiO_3$, $(Ba,Sr)TiO_3$, $BaZrO_3$, $LiNbO_3$, and $BaSnO_3$ **[1]-[7]**. TEM images of selected nanoparticles are given in **Fig. 1**, along with HRTEM images as insets proving the high crystallinity of the nanoparticles. In the case of yttrium oxide, a lamellar nanohybrid was obtained, consisting of crystalline yttrium oxide layers with intercalated benzoate molecules **(Fig. 1d) [8]**.

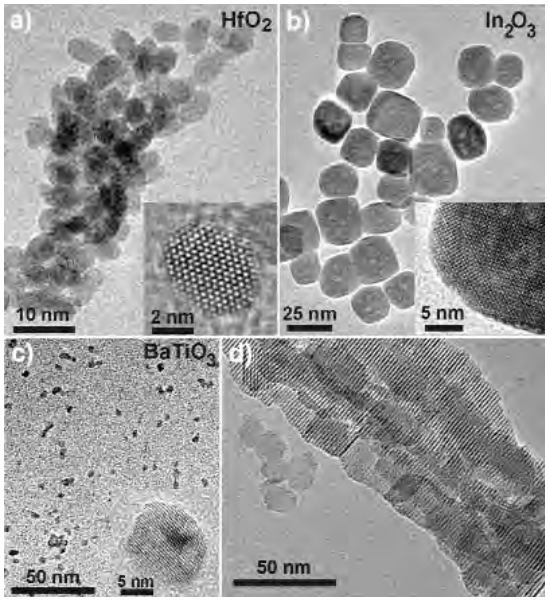

Fig 1: TEM images of a)-c) selected metal oxide nanoparticles and d) yttrium oxide nanohybrid.

Formation Mechanism

The formation mechanism of metal oxide nanoparticles in nonaqueous reaction media is not yet well understood. Therefore, we carefully analyzed the organic species in the final reaction mixtures after removal of the inorganic precipitate to gain some information about possible reaction pathways. The results were surprising and depending on the reaction system, we found several novel reaction mechanisms. For example, in the case of HfO_2 prepared from hafnium alkoxide in benzyl alcohol, nanoparticle formation occurs via ether elimination as shown in **Fig. 2a [4]**. In the case of $BaTiO_3$, which was prepared by dissolution of metallic barium in benzyl alcohol and addition of titanium alkoxide, hardly any ether was found. Instead, the presence of 4-phenyl-2-butanol in stoichiometric amounts gave evidence that the formation mechanism proceeded mainly via a novel pathway involving a C-C bond formation between benzyl alcohol and the isopropanolate ligand **(Fig. 2b) [5]**.

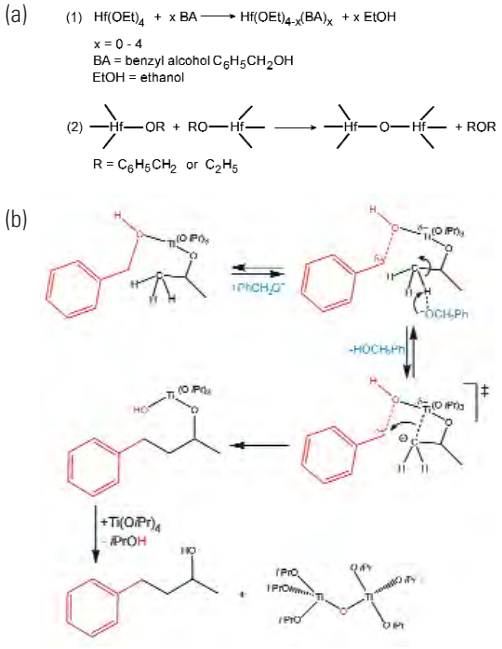

Fig. 2: a) Formation of HfO_2 via ether elimination; b) Formation of $BaTiO_3$ involving coordination of benzyl alcohol, activation of the benzylic carbon atom via weakening of the C-O bond, deprotonation of the β-carbon atom of the isopropoxy ligand, nucleophilic attack leading to 4-phenyl-2-butoxide formation and OH, finally condensation and elimination of 4-phenyl-2-butanol.

Nanoparticle Assembly

The controlled organization of the metal oxide nanoparticles into well-defined nanostructures was achieved by two different approaches, either via specific surface functionalization of the nanoparticles or via polymer-directed assembly.

Following the first strategy, we synthesized titania nanoparticles in the presence of a small amount of 2-amino-2-(hydroxymethyl)-1,3-propanediol [$(HOCH_2)_3CNH_2$, Trizma]. Upon redispersion of the Trizma-functionalized titania nanopowder in water, the nanocrystals start to assemble into highly anisotropic arrangements (**Fig. 3a**, inset) **[9] [10]**. HRTEM shows that these pearl-necklace structures consist of perfectly oriented nanoparticles forming a pseudo-single crystal along the [001] direction **(Fig. 3a)**. The polymer-directed assembly of crystalline cerium oxide nanoparticle sols **[11]** resulted in the formation of highly ordered, 3D mesoporous materials **(Fig. 3b) [12]**. Similar results were obtained with SnO_2 nanocrystals **(Fig. 3c)**.

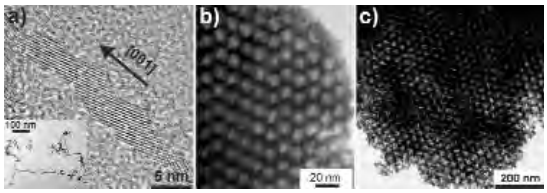

Fig. 3: TEM images of nanoparticle assemblies. a) TiO_2 nanowires, b) mesoporous CeO_2, and c) mesoporous SnO_2 (after calcination).

Applications

Some of the prepared metal oxide nanoparticles such as SnO_2 and In_2O_3 are promising candidates for gas sensing devices. In order to test the sensing properties of these nanopowders, sensor devices were fabricated by deposition of thin films of the respective nanopowders dispersed in water onto alumina substrates (details are given in **Fig. 4**). The front side of the substrate is equipped with gold contacts and on the backside is a platinum heater. The measurement of the electrical current in dependence of gas flow showed that the nanopowders exhibited high sensitivity and good recovery time. Especially the indium oxide nanoparticles were highly sensitive towards NO_2 with a detection limit of 1 ppb at low temperature **[6]**.

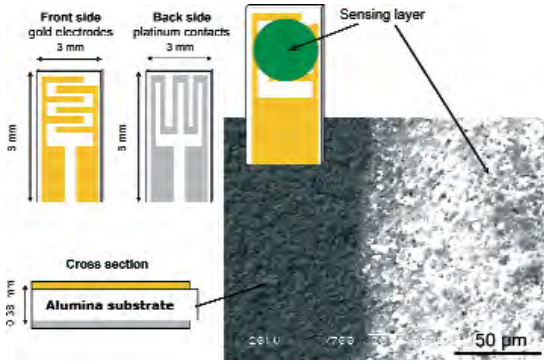

Fig. 4: Design of a gas sensing device.

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Fractionating Colloid Analysis

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As in the years before, Analytical Ultracentrifugation (AUC) and Field-Flow Fractionation (FFF) were available as an active and versatile service unit for a large variety of colloid and polymer analysis problems from the institute and external cooperation partners **[1-5]**. Special emphasis was laid upon the investigation of new particle properties by AUC. We could reveal that AUC is very sensitive to the nanoparticle surface structure in terms of charges by clearly distinguishing between TiO_2 particles of very similar size and shape but different exposed crystal faces **[6]**. This implies that AUC should be capable to determine particle charge distributions in addition to particle size distributions in the future, but the basic theory for the treatment of such experiments is still missing.

Also, we were able to show that the complete dependence of the spectral properties of quantum size nanoparticles can be determined in a single AUC run on a polydisperse sample **[7] (Fig. 1)**. Up to now, such dependencies had to be elucidated via the tedious synthesis of monodisperse nanoparticles of various sizes with subsequent spectral characterization.

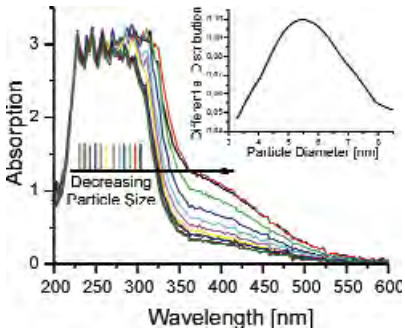

Fig. 1: AUC measurements showing UV-Vis absorption spectra of dopamine-functionalized titania nanoparticles dependent on the particle size fractions. Inset: particle size distribution curve of dopamine functionalized titania nanoparticles.

For very complex systems, one fractionating technique alone cannot yield the full information about the system. One example of such system is ferritin, which is consisting of different oligomers, each of which is filled with varying amounts of iron oxide. Thus, ferritin has a particle size distribution superimposed with a density distribution. Flow-Field-Flow Fractionation (Fl-FFF) can yield the particle size distribution as this technique is independent of the particle density **(Fig. 2)**.

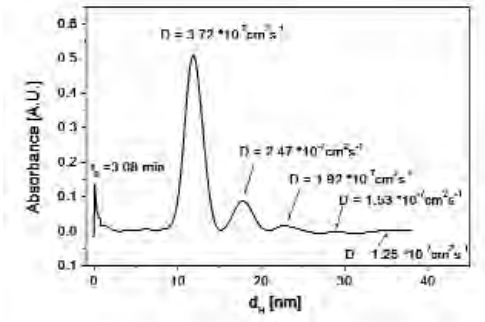

Fig. 2: Fl-FFF elugram of ferritin after conversion to particle size distribution.

Analytical ultracentrifugation on the other hand is dependent on particle size and density so that the corresponding distribution is more smeared as compared to that from Fl-FFF **(Fig. 3)**.

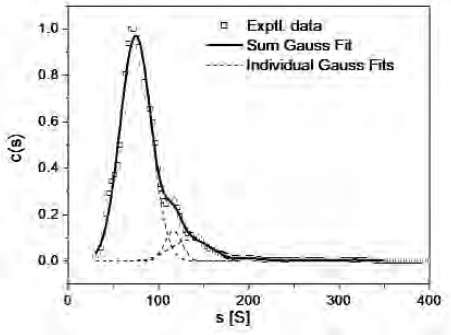

Fig. 3: Diffusion-corrected s distribution of ferritin from AUC.

However, the combination of the sedimentation and diffusion coefficient data from both techniques yields additional information like the buoyant molar mass and the solution shape of the different oligomers **[8]**. Although this analysis was only performed for the peak maxima, combination of the whole distributions could in principle yield distributions like molar mass and density distributions in such global analysis approach for experiments performed in different solvents.

Improved detectors are important for a sophisticated analysis of the increasingly complex colloidal systems. In cooperation with BASF AG, we have developed a fast fiber based UV/Vis detector for the Analytical Ultracentrifuge. This detector has several advantages: 1) Very fast detection down to 2 ms compared to several minutes for the current commercial design, 2) Simultaneous detection of the whole UV/Vis wavelength range (200 – 1000 nm) opening up a further dimension with the associated analytical information 3) Modular design adaptable to every preparative ultracentrifuge. The increased information of the three dimensional data space as compared to the two dimensional detection with commercial instruments is visualized for one scan in **Fig. 4**.

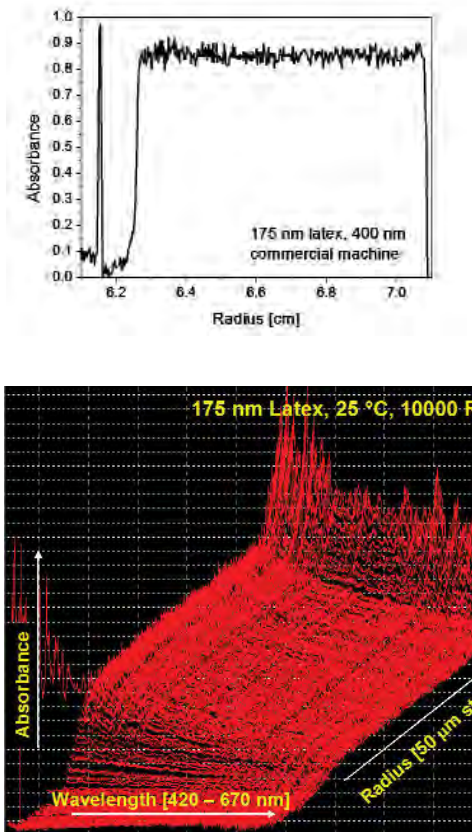

Fig. 4: Single Scan for a sedimenting latex with the commercial instrument (upper) and the developed fibre optics detector (lower)

In the example shown in **Fig. 4**, the wavelength dependence of the detected turbidity contains information about the particle size so that in the future, colloid density distributions may become available simultaneously to particle size distributions. The multiwavelength detector should also prove valuable for interaction studies of compounds with dissimilar chromophores. The first prototype was developed and installed and is currently tested for sophisticated applications. Also the hard- & software is further improved.

These developments indicate a new trend in fractionating colloid analysis: Multidetector application and global analysis of experiments with various physicochemical techniques like AUC combined with FFF.

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Electron Microscopic Studies of Colloidal Systems and Biomaterials

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Transmission and scanning electron microscopy are powerful analytical tools to investigate the relationship between the morphological structure and the physical properties of colloidal systems and biomaterials on the one hand and the relationship between their synthesis conditions and morphological structure on the other hand. Because of the structure of the institute, we are working together with a number of groups in the colloid chemistry, interface and the biomaterials departments. Our research activities are focussed on the electron microscopic exploration of the morphological structure of polymer micelles and particles, inorganic crystals, biominerals, polyelectrolyte complex shells and biomaterials. Some interesting results are presented here.

Templating techniques are used for the controlled formation of highly porous materials with a defined structure and desired properties, which are interesting for analytical applications, photonics and catalysis. Colloidal crystals, polymer gels, porous inorganic microspheres and polymer particles are suitable templates for the synthesis of new inorganic (e.g. silicon dioxide) or specific organic networks (e.g. molecularly imprinted polymers). The empty space of a colloidal crystal of polystyrene particles can filled, e.g. with a mixture of an amphiphilic ionic liquid and tetramethylorthosilicate, used as the sol-gel precurser. To control the synthesis processes of the three-dimensional structural hierarchies both the structures of ordered latex spheres and the final pore structure of silica skeleton after calcination the materials are characterized by electron microscopy. **Fig. 1** reveals that the removal of both templates did not destroy the original ordered structure replicated into the inorganic matrix. The interconnected network of the spherical voids left in the silica was still arranged in wellordered close-packed structures. The average size of the voids and thickness of the walls are about 175 nm and 25 nm, respectively, the void size is slightly smaller than that of the PS sphere, due to shrinkage during calcination. Further TEM investigations shows that the wall architecture is made up of larger domains of a ordered nanoporous lamellar phase surrounding the macropore. The interlayer periodicity of the lamellae is about 2.7 nm, with ca. 1.3 nm thick slit pores and 1.4 nm thick walls, respectively.

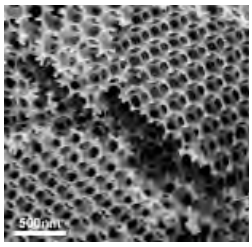

Fig.1 : Tailored bimodal three-dimensional order of porous silica after calcination

Mesoporous silica materials are suitable materials for the examination of nanoreactor effects. For their synthesis the so-called nanocasting process was used where different template phases are transferred to the pores in a 1:1 imprinting process. Depending on the templates, different pore sizes can be achieved. Cyclodextrins lead to pores between 1.5 nm and 2 nm, nonionic surfactants or mixtures of them lead to pores between 2 nm and 4 nm, and poly(styrene)-poly-(ethyleneoxide) block copolymers (SE) result in pore diameters between 4.5 nm and 10 nm **(Fig. 2)**.

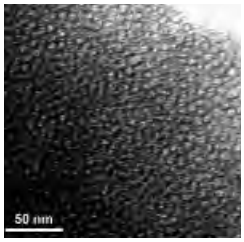

Fig. 2: Mesoporous structure of SE-based silica material

One of the main projects is the electron microscopic investigation of biomimetic synthesized inorganic minerals with complex forms. Organic additives and/or templates with complex functionalization patterns are used to control the nucleation, growth, and alignment of inorganic crystals. It is possible to stabilize the $PbCO_3$ platelet-like intermediates permanently by increasing the binding strength of double hydrophilic block copolymers.

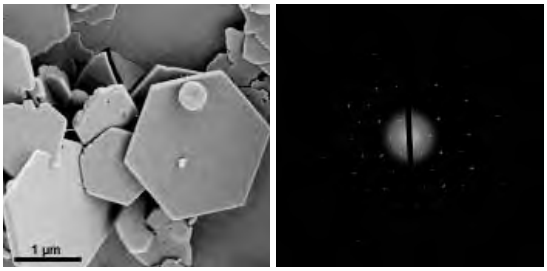

Fig. 3a: $PbCO_3$ nanoplates with a quasi-hexagonal crystal morphology
Fig. 3b: Electron diffraction pattern of the $PbCO_3$ plates

Thin platelet-like particles with a smooth surface and a thickness of about 90 nm are growing, if the strong binder PEG-*b*-[(2-[4-dihydroxy phosphoryl]-2-oxabutyl)acrylate ethylester] (1 g L^{-1}) is used. **Fig. 3a** reveals the morphology of $PbCO_3$ particles, formed after two weeks at room temperature and pH = 5. The electron diffraction pattern **(Fig. 3b)** taken along ⟨001⟩ shows its single crystalline nature, corresponding to uniaxially elongated quasi-hexagonal thin plates.

Low molecular weight polyelectrolytes can be used for the self-assembly of complex spherical $BaCO_3$ superstructures through a facile mineralization process under ambient conditions. Without adding polymer additives and through either rapid mixing or slow gas diffusion dendritic growth of $BaCO_3$ occurs. In **Fig. 4a** the morphology of $BaCO_3$ particles are shown synthesized by a mineralization reaction for two weeks at room temperature (pH = 5, [$BaCl_2$] = 10 mM). Energy-dispersive X-ray analysis confirms the stoichiometric molar ratio for $BaCO_3$. However, mineralization in the presence of 1 g L^{-1} poly(styrenesulfonate) (PSS) produced well-

defined $BaCO_3$ microspheres with a diameter in the range of 2 - 3.5 µm **(Fig. 4b)**. They were built from smaller, elongated rodlike building blocks with a typical diameter of 50 nm and length of 200 nm, which apparently adopted the more equilibrated isostructural aragonite appearance.

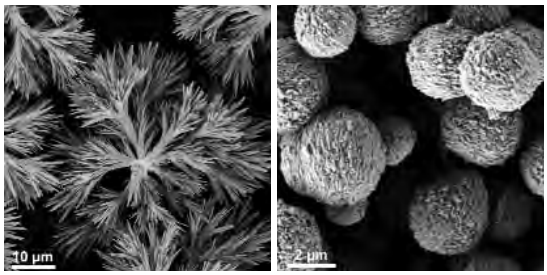

Fig. 4a: Dendritic $BaCO_3$ crystals without additives
Fig. 4b: $BaCO_3$ microspheres in the presence of PSS

Colloidal crystals have been extensively explored as model systems of condensed matter physics. The actual research is devoted to the design and controlled fabrication of non-close packed 2D colloidal crystals on silica wafers via dip-coating. Different from the routine colloidal crystallization procedures swollen polymer hydrogel spheres are used as building blocks. As basic colloids poly(N-isopropylacrylamide) (PNIPAM) latex particles with an hydrodynamic diameter of 670 nm are employed. In addition to the original PNIPAM dispersion the in situ mineralization of $CaCO_3$ in the hydrogel particles was used for the fabrication of a $CaCO_3$/PNIPAM composite spheres. If the reduction of the inter-sphere distance is smaller than the shrinkage of the individual spheres, the non-close packing arrays on solid surfaces can be formed. **Fig. 5** reveals a typical 2D colloidal crystal produced by dip-coating of a 0.1 wt-% $CaCO_3$/PNIPAM composite dispersion at a withdrawing speed of 5 µm/s. The non-close packing array consist of disc-like particles of around 550 nm in diameter and the center-to-center distance between particles is about 1040 nm, corresponding to a 490 nm interparticle gap, which is similar to that derived from the pure PNIPAM spheres.

This may likely be due to the fact that the loading amount of $CaCO_3$ is quite low. If the withdrawing speed is reduced to 1 µm/s, the center-to-center distance between particles decreases to 730 nm, correspondung to a 180 nm gap between the particles. The exploration of the mechanisms behind the formation of 2D non-close packing arrays based on hydrogel spheres is an ongoing project in the interface department.

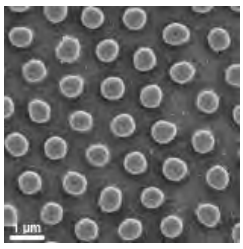

Fig. 5: Typical 2D colloidal crystal structure of $CaCO_3$/PNIPAM composite

Hierarchically structured biomaterials, e.g. grasses, bamboo, and bones, with a high mechanical performance may serve as models for the development of biomimetic materials.

In cooperation with the biomaterials department we are interested in the silica distribution in horstail Equisetum hyemale, which can be used as model plant for biomineralization and biosilicification. To determine the location of the accumulated silicon we examine cross sections of various significant horstail structures using scanning electron microscopy for structural and analytical investigations **(Fig. 6a)**. Energy-dispersive X-ray spectroscopy and elemental mapping of silica was done to identify positions where silica is concentrated.

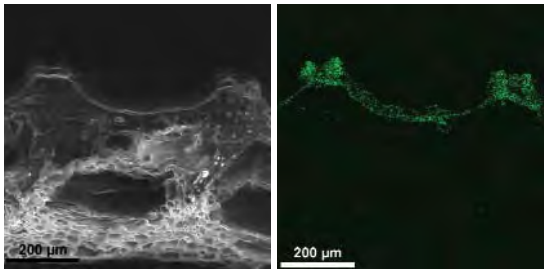

Fig. 6a: Cross-section of the stem of the horstail
Fig. 6b: Silicon distribution in the region of Fig. 6a

In general the silica is localized as a thin layer on the outer surface. It seems that the silica can not enter the cell membranes and remains concentrated on the surface **(Fig. 6b)**. The thickness of the silica layer varies in the range of 3 µm to 15 µm.

Another project is the investigation of the mineral-collagen composite structure of cattle femur at the nano-structural level to determine the degree of mineralization. A special embedding technique for the oriented fixation of the biomaterial structure was developed. The ultra-thin cross-section **Fig. 7** reveals that the mineral is embedded in the fibrilar collagen structure. In certain localized areas circular oriented mineral pattern are observed. The crystals have a platelet-like shape with irregular edges and the crystal size range in length from 15 nm to 150 nm, in width from 10 nm to 80 nm, and in thickness from 2 nm to 6 nm.

In the future more detailed investigations the crystal shape, size, order and the location of the minerals in dependence on the degree of mineralization are of special interest.

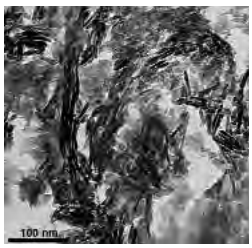

Fig. 7: Ultra-thin cross-section of a mineralized cattle femur

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Multi Angle Laser Light Scattering in Dependence on Time

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Aggregation and disaggregation processes of supermolecular structures often take place in time intervals, which interfere with the time needed for a measurement of the angular dependence scattering curve by goniometer type LS instruments. This results in inconsistent scattering curves as measurements for different angles are taken at different times.

MALLS may solve this problem by simultaneous measurement of the intensity for the entire angle range. This way complete scattering curves vs. time can be produced.

The MALLS instrument DAWN EOS (Wyatt, USA), designed and mainly used as detector for online measurements with a flow cell after fractionation methods (GPC or FFF) has been modified in our lab. The combination of the advantages of the DAWN instrument, the introduction of an index-matching bath and additional equipment to improve the accuracy of measurements and further development of our software package LISA yields an effective tool.

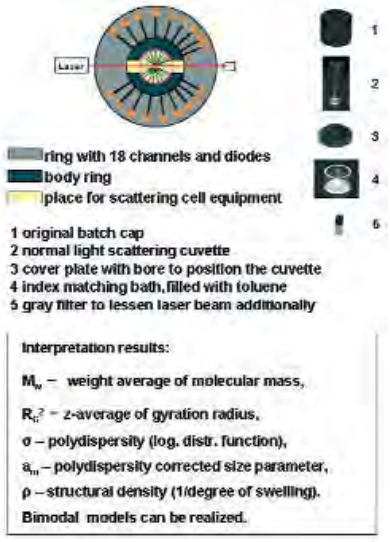

Fig. 1: Scheme of the sample room, additional equipment, general results

Polyelectrolyte Complexes – Subsequent Addition of Salt

Polyelectrolyte complexes (PECs) are of high practical relevance, ranging from large-scale industrial use up to special purposes in biotechnology and medicine. An important feature in all applications is their sensitivity to environmental changes, especially alteration of salt conditions. During the addition of sodium chloride, PECs with carboxylic groups containing polyanions show swelling, aggregation and finally dissolution at a critical salt concentration. Such processes were studied in detail by MALLS.

Materials: PEC Cop47/NaPMA, polyanion: NaPMA, polycation: Cop47 (a copolymer of diallyldimethylammonium chloride and acrylamide with 47 mol-% of cationic groups), PEC prepared in pure water, mixing ratio X=0.6

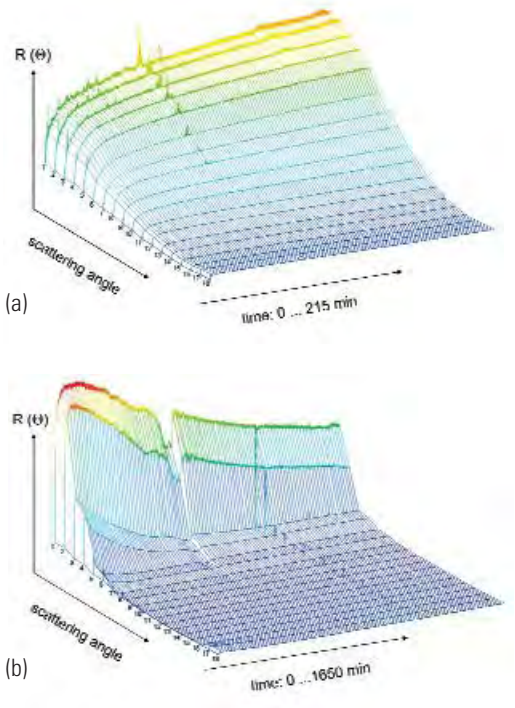

Fig. 2: Scattering curves recorded after adjustment to an ionic strength of 0.4 (a) and 0.475 N NaCl

Steps: (1) start with PEC in light scattering cuvette – characterization in pure water,
(2) addition (very fast under vigorous stirring) of a 2N NaCl solution, immediately inserting the cuvette into the DAWN instrument (delay time about 10 sec),
(3) light scattering studies in dependence on time.

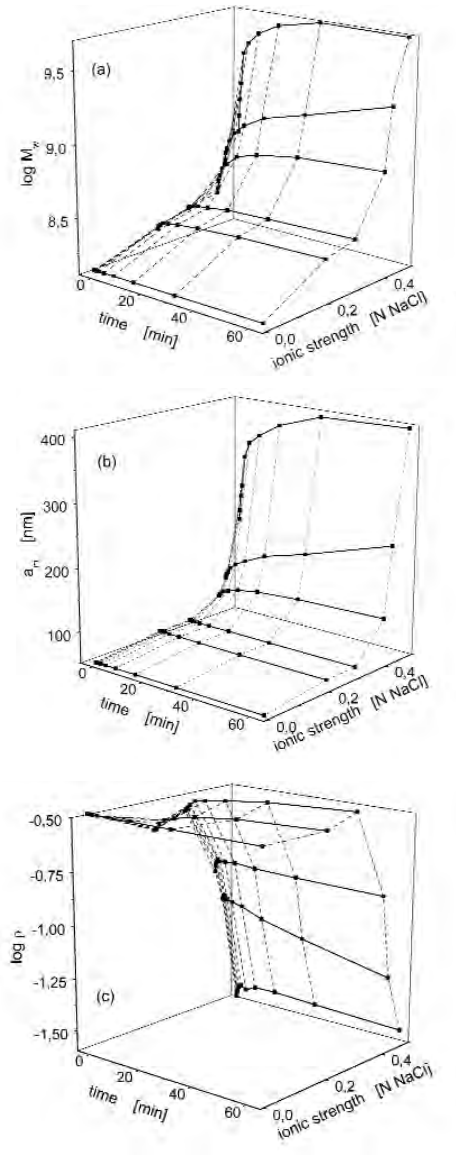

Fig. 3: Time dependence (64 min) of (a) particle mass Mw, (b) polydispersity corrected radius a_m, (c) structure density ρ at different ionic strength (0, 0.2, 0.3, 0.4, 0.425, 0.475 N NaCl)

Aqueous Heterophase Polymerization of Styrene

Online MALLS experiment, addition of initiator to a styrene solution in water.

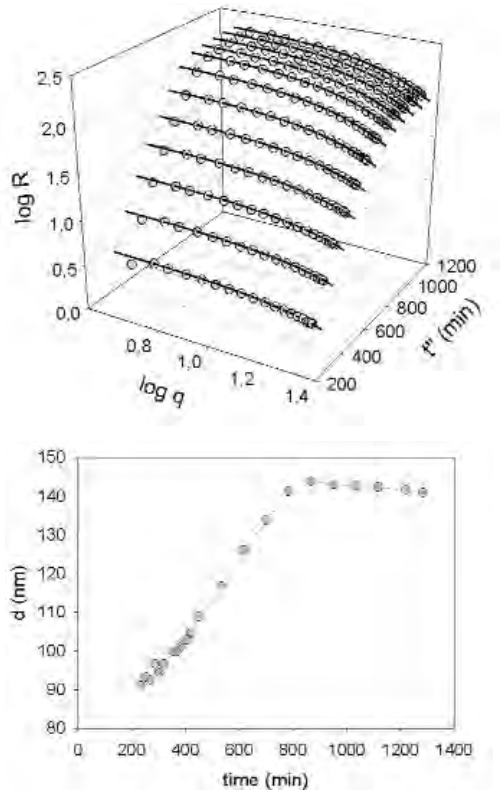

Fig. 4: (a) Scattering curves during predominant particle growth, symbols – experimental points, solid lines – adequate interpretation models; time after the addition of initiator, (b) average size (spheres, diameter) of the colloidal particles

Conclusion

A detailed analysis of the scattering curves provided the structural parameters particle mass, radius and structure density and offers the chance to distinguish between the time dependence of the processes of swelling, secondary aggregation and complete dissolution of the PEC particles.

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Modern Methods of Light Scattering

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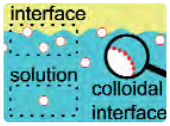
1998-2000: Postdoc (Institute of Electronic Structure and Laser, Heraklion, Crete, Greece)
Since 2000: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)



Light scattering measurements are versatile and well-established tools for the investigation of colloids and polymers in solution. With special polarization dependent experiments or total internal reflection geometry, the scattering experiments become sensitive to interfacial properties. The target of the research is to develop new methods and apply them to questions concerning the physics of colloidal particles and polymer aggregates.

Ellipsometric Light Scattering

By combining a light scattering experiment with polarization optics of an ellipsometer, a new technique has been established for the investigation of the interface of colloidal particles to the surrounding solvent. While classical reflection ellipsometry detects a thin layer on a flat interface, ellipsometric light scattering characterizes thin layers on spherical colloidal particles. Experiments on different colloidal systems have been performed in collaboration with the group of Klaus Tauer.

As an example, **Fig. 1a** displays data for colloids with a corona composed of poly-electrolyte chains (sodium polystyrene sulfonate). Here, Θ is the scattering angle and $\tan(\Psi)$ and Δ are the measured ellipsometric parameters (amplitude ratio and relative phase difference of the scattering amplitudes for two polarization modes). Similar to reflection ellipsometry, the information about the refractive index profile at the interface is encoded in the shape of $\tan(\Psi)$ and Δ and has to be determined in a fitting procedure. For the poly-electrolyte corona, the profile of the refractive index difference to the solvent follows a power law with the exponent α. Data for α obtained from simultaneous fit of measurements at the available two wavelengths of light (532nm and 633nm) are

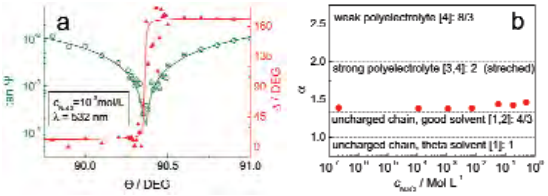


Fig. 1: Ellipsometric light scattering on colloidal particles with a poly-electrolyte corona. (a) Raw data. (b) Exponent α of the power law describing the refractive index profile.

displayed in **Fig. 1b**. The comparison to different theories shows, that α corresponds to the value for uncharged chains, independent of the concentration c_{NaCl} of the added sodium chloride salt. The stretching of the poly-electrolyte chains by electrostatic interactions or osmotic pressure of the low molecular weight counterions (not shown here) does not affect the exponent of the refractive index profile.

Another experiment with an unexpected result is the behaviour of charged colloidal particles at different concentrations c_{NaCl} of added salt. Raw data for $\tan(\Psi)$ are displayed in **Fig. 2a**. There are two regimes at low and high c_{NaCl}. Experimental data for different c_{NaCl} overlap within the regimes, respectively, but there is a transition between the two regimes at around the $c_{NaCl}=10^{-4}$mol/L. While the $\tan(\Psi)$ and Δ data for two wavelengths of light are well described by a model of a homogenous sphere at low c_{NaCl}, a reasonable fit in the high c_{NaCl} regime requires the introduction of an additional layer at the interface of the colloid. The nature of the layer is not clear yet.

Since ellipsometric scattering is affected by birefringence within a particle shell, it was possible to determine the order of lipid vesicles. Experiments on colloidal particles with a corona of polymers with thermo-responsive solubility

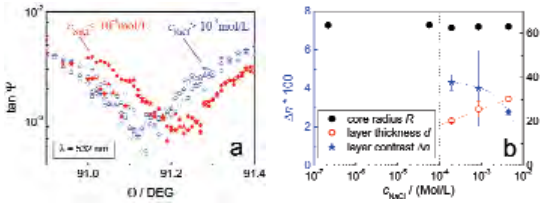
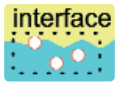


Fig. 2: Ellipsometric light scattering on charged colloids. (a) Data for $\tan(\Psi)$ at several salt concentrations c_{NaCl}. (b) Core radius R, shell thickness d and contrast factor Δn obtained from the fitting procedure.

(Poly-[N-isopropylacrylamide, PNIPAM]) indicate that the thickness resolution of ellipsometric light scattering with two wavelength of light is better than 20nm. For improved accuracy, a new multi wavelength apparatus is under construction. Other future plans concern – beside the application of the technique to different samples – the experimental and theoretical investigation of effects of particle interaction, multiple scattering, and non-spherical particle shape.

Procedures of Interface Light Scattering



Although a liquid-liquid interface is of special interest for exchange processes and interface fluctuations, it is much less investigated than other types of interfaces. For transparent solvents (e.g. oil and water), various properties of the interface can be determined by non-perturbing optical methods. Reflection ellipsometry gives the average surface concentration of dissolved colloids or polymers, while capillary wave spectroscopy yields the interface tension. In a total-internal-reflection geometry, the solvent of lower refractive index is illuminated only by the evanescent wave, which penetrates just a fraction of the wavelength. The scattering of this light contains information about amplitude and dynamics of fluctuations close to the interface. A home-built apparatus for all three experiments is shown in **Fig. 3**.

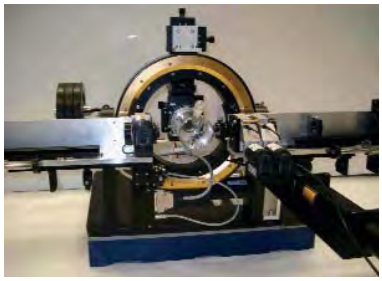


Fig. 3: Home-built apparatus for ellipsometry, evanescent wave scattering and capillary wave spectroscopy at the liquid-liquid interface.

A first project is the investigation of the interface behaviour of colloidal particles with pH-dependent amphiphilicity, in collaboration with the group of Steve P. Armes (University of Sussex, UK). Ellipsometry yields the height of the particles within the interface and the interface concentration. While at the water-air interface the colloids form a sub-monolayer with decreasing interface concentration at higher temperature, the water-oil interface is covered with a double layer where the interface concentration increases with temperature (see **Fig. 4**). The pH-dependent height reflects the change of contact angle.

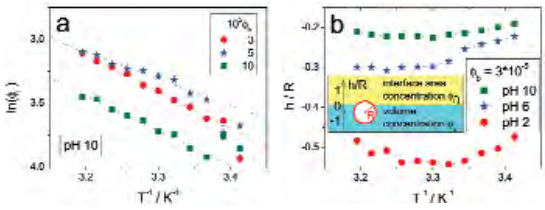
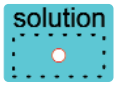


Fig. 4: Colloids with pH-dependent amphiphilicity at the water-dodecane interface. (a) Interface concentration φ_i. (b) Heigth in the interface.

Results Obtained by Classic Static and Dynamic Light Scattering



The aggregation behaviour of simple block copolymer samples in a selective solvent is well understood in terms of geometrical packing arguments. The incorporation of specific interactions like H-bridges of polypeptides or electrostatic attraction of opposite charges into block copolymer samples changes the structure of the aggregates significantly. In collaboration with the group of Helmut Schlaad, their synthetic activity was complemented by structure analysis of aggregates in solution by combined static and dynamic light scattering.

As an example, **Fig. 5** displays experimental data for a block copolymer including a poly peptide block (1,2-polybutadiene-*block*-poly[L-lysine]). In water, the polymer forms wormlike aggregates. The switching of the peptide conformation from a gaussian coil (pH 7) to a helix (pH 10) induces a change in the linear packing density: the value of the dotted line at low values of the scattering vector q indicates the number of polymers per nanometer.

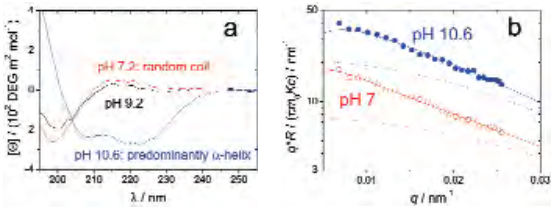


Fig. 5: Wormlike aggregates of block copolymers with a polypeptide block. (a) pH-dependent conformation of the poly peptide determined by circular dichroism. (b) Holtzer plot of the specific scattering intensity $R_\Theta/(Kc)$ normalized with the molecular mass m_0 of a single polymer. The dotted line indicates the asymptotic behaviour due to the finite worm thickness, calculated from the fit parameters.

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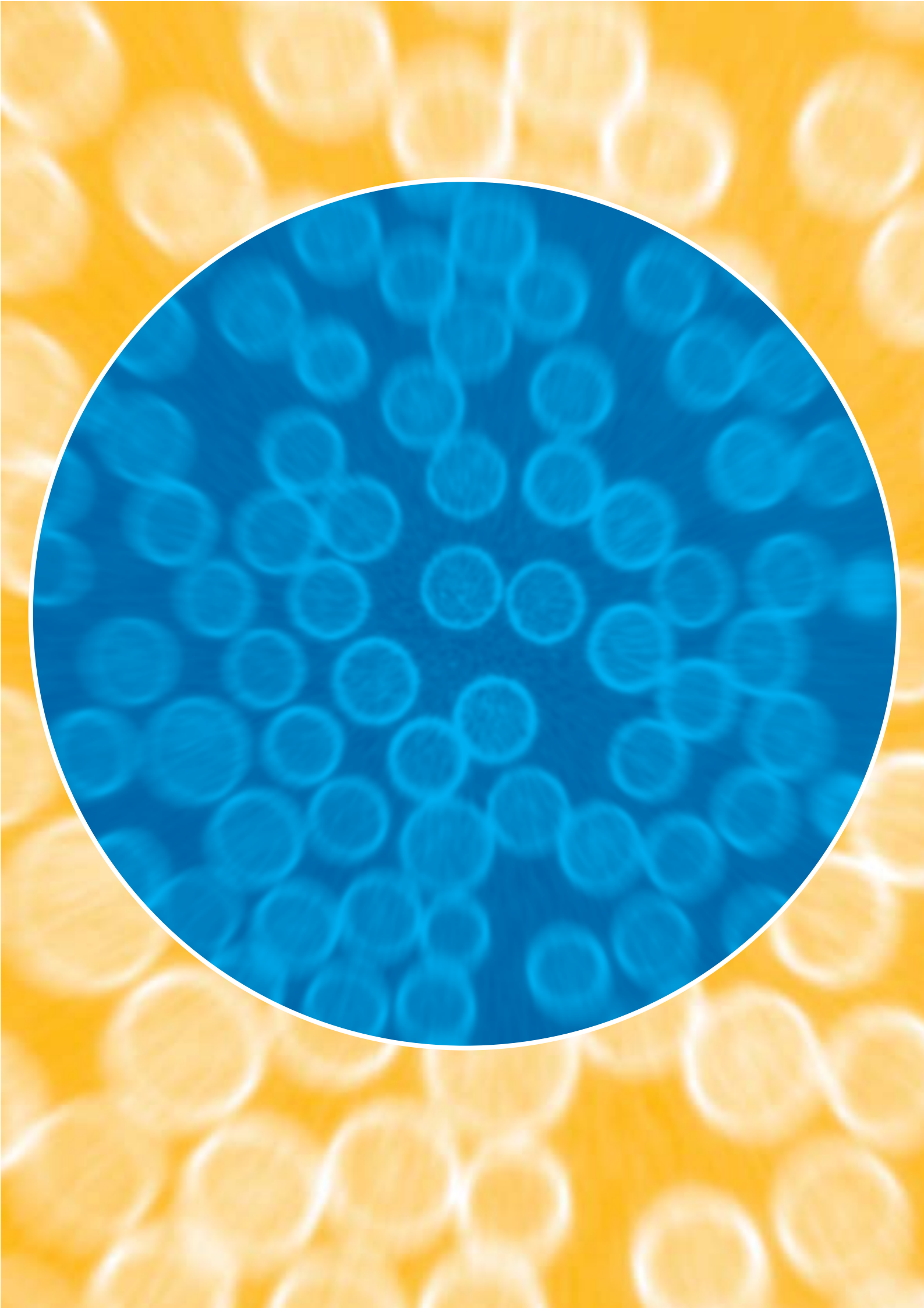
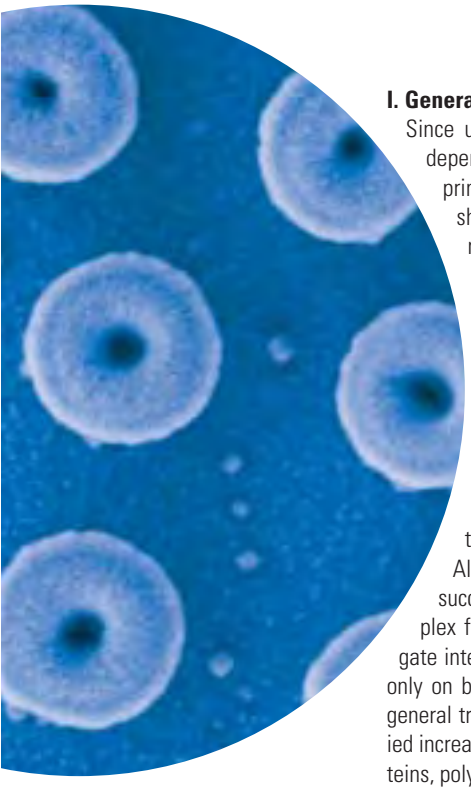
INTERFACES



Research in the Department of Interfaces



I. General Strategy

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

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

II. Research Highlights

II.1 Planar Interfaces

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

II.2 Nonplanar Interfaces and Complex Films

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

III.3 Cooperations

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

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

IV. Past and Future Development

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

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

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

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

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

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

Helmuth Möhwald
Director of the Department of Interfaces

Interactions in Complex Monolayers

Gerald Brezesinski 02.04.1950
1974: Diploma, Biophysics (Lomonossow University of Moscow) Thesis: The parametric pump – a physical-chemical model of the active transport of ions in cells
1981: PhD, Physical Chemistry (Martin Luther University of Halle/S.) Thesis: Einfluss der chemischen Struktur auf das thermische Phasen- und Mischungsverhalten binärer und ternärer Phospholipid-Wasser-Systeme
1987: Habilitation, Colloid Chemistry (Martin Luther University of Halle/S.) Thesis: Untersuchungen zum Phasen- und Mischungsverhalten ausgewählter Phospholipid-Wasser-Systeme
1981-1982: Postdoc (Biological Research Centre, Szeged, Hungary)
1982-1992: Research Scientist (Institute of Physical Chemistry, University of Halle/S.)
1992-1995: Research Scientist (Institute of Physical Chemistry, University of Mainz)
Since 1995: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Nonviral DNA Transfection

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

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

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

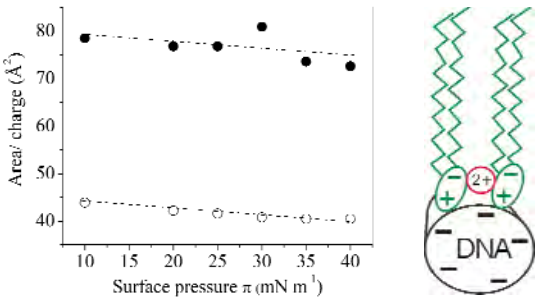


Fig. 1: (left) Area per elementary charge as function of surface pressure π of calf thymus DNA (●) and DMPE (○) as deduced from GIXD. (right) Schematic representation of DNA–DMPE interaction mediated by divalent cations

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

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

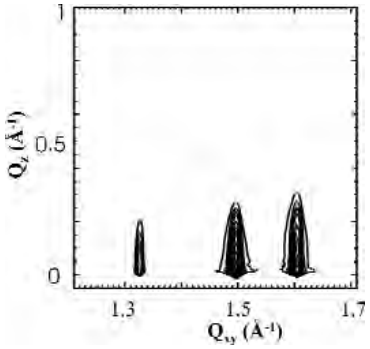


Fig. 2: Contour plots of the corrected X-ray intensities as function of the in-plane (Qxy) and the out-of-plane (Qz) scattering vector components of N-(2-aminoethyl)-N´-2-dihexadecylpropanediamide taken at 20 mN/m and 20 °C.

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

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

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

Results: Due to its amphiphilic character Amyloid beta (1-40) peptide adsorbs to the air/water interface and penetrates into weakly compressed lipid monolayers. Langmuir monolayers of negatively charged as well as of zwitterionic phospholipids have been used to study the influence of the pep-

tide on the lipid packing and vice versa the influence of the lipid on the peptide secondary structure by means of IRRAS and GIXD. Being adsorbed at the interface, the peptide adopts beta-sheet conformation oriented parallel to the surface **(Fig. 3)**.

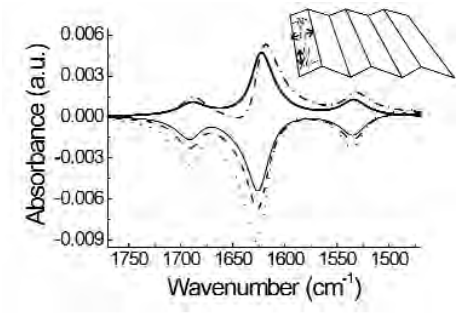


Fig. 3: Simulation of IRRA spectra (p-polarized light, angle of incidence between 32° and 62°, Amide I bands at 1627 and 1690 cm^{-1} and the Amide II band at 1535 cm^{-1}) of a beta-sheet secondary structure lying flat at the air/water interface. The measured spectra agree very well with the simulated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

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

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

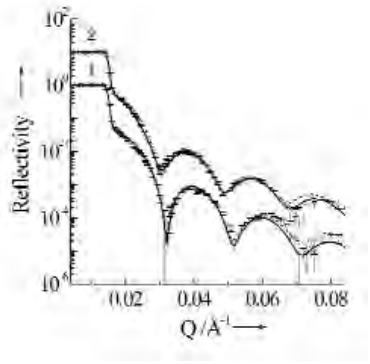


Fig. 4: Neutron reflectivity of a charged PEI/(PSS/PAH)$_6$ film in D_2O: 1) bare polymer surface; 2) polymer surface exposed to Amyloid beta (1-40) peptide solution for 12 h. The curves are offset for clarity.

Enzymatic Reactions at Interfaces

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

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

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Key Publications:

[1] Symietz, C., Schneider, M., Brezesinski, G. and Möhwald, H.: DNA-alignment at cationic lipid monolayers at the air/water interface. Macromolecules **37**, 3865-3873 (2004).
[2] Gromelski, S. and Brezesinski, G.: Adsorption of DNA to zwitterionic DMPE monolayers mediated by magnesium ions. PCCP **6**, 5551-5556 (2004).
[3] Maltseva, E. and Brezesinski, G.: Adsorption of Amyloid beta (1-40) peptide to phosphatidylethanolamine monolayers. ChemPhysChem **5**, 1185-1190 (2004).

Thin Liquid Films

Regine v. Klitzing 05.12.1966
1992: Diploma, Physics (Göttingen University)
Thesis: Studies on the Psychoacoustic Overshoot Effect
1996: PhD, Physical Chemistry (Mainz University)
Thesis: Adsorption of Polyelectrolytes at Charged Interfaces, Molecular Transport and Ion Distribution within Polyelectrolyte Multilayers
1996-97: Postdoc, (CNRS-CRPP, Pessac, France)
1998-2003: Assistant Professor, (Stranski-Laboratorium, TU Berlin)
2003: Habilitation, Physical Chemistry (TU Berlin)
Thesis: Structuring of Polyelectrolytes in Thin Films and Near Interfaces
2004: Group Leader, (Max-Planck Institute of Colloids and Interfaces, Potsdam)
Acceptance of Heisenberg Fellowship
Since 2004: C3-Professor, Physical Chemistry (Kiel University)

Aims

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

Results

Intermolecular Interactions

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

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

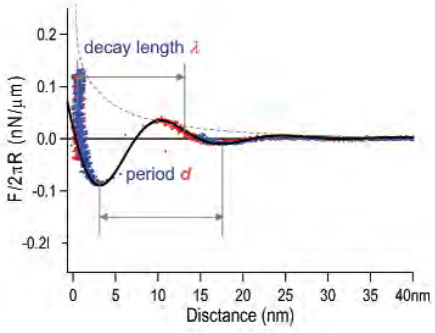

Fig. 1: Exemplary image of an oscillatoric force curve of an aqueous polyelectrolyte film confined in a Colloidal-Probe AFM.

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

Intramolecular Interactions

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

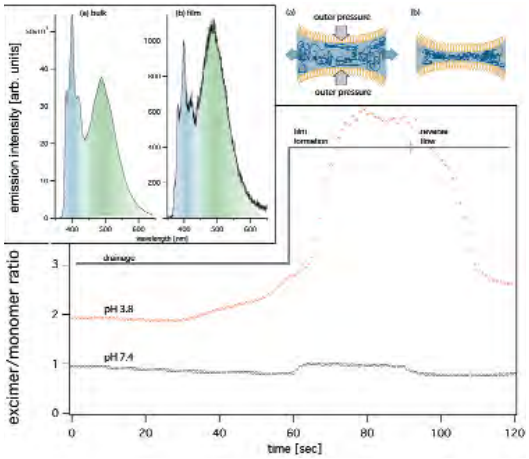

Fig. 2: Left hand side: Fluorescence spectrum of aqueous SDS/Py-PAA solution in the bulk phase and in a foam film. Right hand side: Excimer/Monomer ratio during the increase of the outer pressure (film formation) and pressure decrease (reverse flow) for two different pH.

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

Effect of Surface Modification

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

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

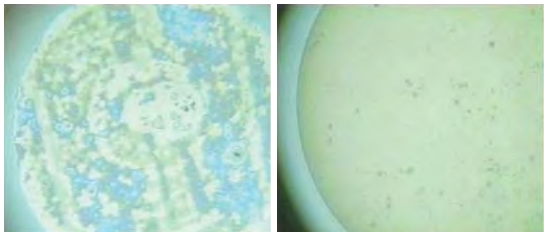

Fig. 3: Aqueous films on top of modified Silicon substrates: unstable on Si/ PEI (left), stable on Si/PEI/PSS (right).

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

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

Polyelectrolyte Multilayers as Coatings

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

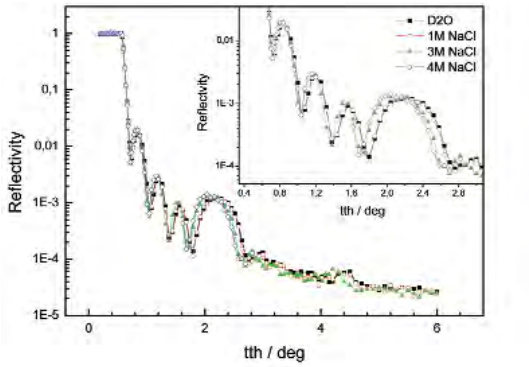

Fig. 4a) D_2O swollen PSS/PAH multilayer with a d-PSS superlattice at different outer ionic strengths (adjusted with NaCl) – in collaboration with Roland Steitz, HMI, Berlin

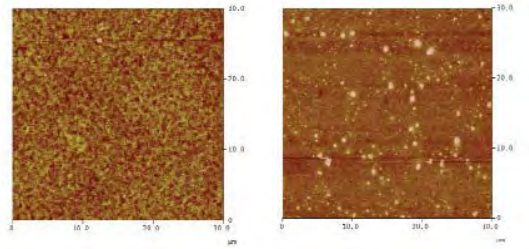

Fig. 4b) AFM micrographs of a PSS/PDADMAC multilayer exposed to 1 Mol/l (left) and to 2.5 Mol/l aqueous NaCl solutions (right).

Future Work

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

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Key Publications:

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

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

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

Thermodynamics of Thin Layers

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Aims

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

Results

Effect of the Applied Pressure on the Film Stability

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

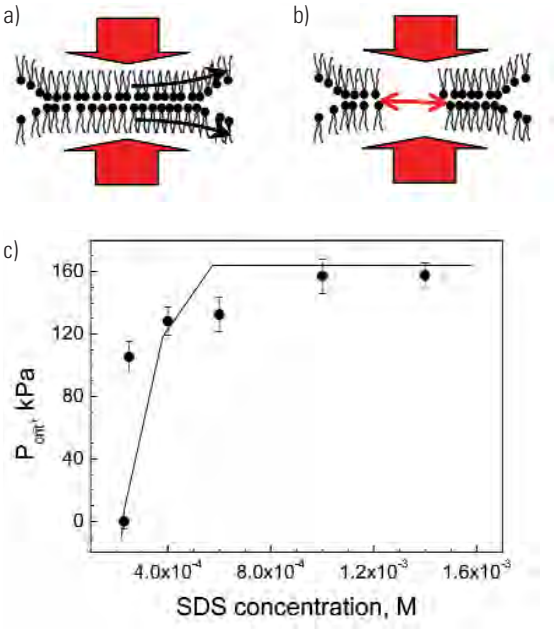

Fig. 1: a) Desorption of surfactant molecules from the NBF surfaces as a result of increased external pressure; b) NBF with formed critical hole which spontaneously grows and the film ruptures; c) Experimental data (●) and theoretical predictions for the critical rupture pressure as a function of the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

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

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

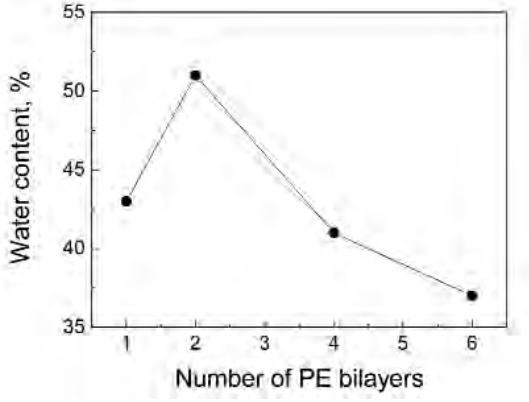

Fig. 2: Water content as a function of the number of PE bilayers

Future Work

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

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Key Publications:

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

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

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

Thermodynamics, Kinetics and Dilational Rheology of Interfacial Layers

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Aims

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

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

Thermodynamics of Adsorption Layers

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

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

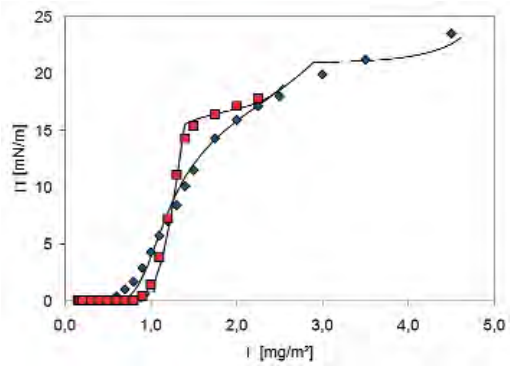

Fig. 1: Dependence of surface pressure Π on adsorption Γ, for β-casein (◆) and BSA (■), points are experimental data, curves calculated from the new model [1]

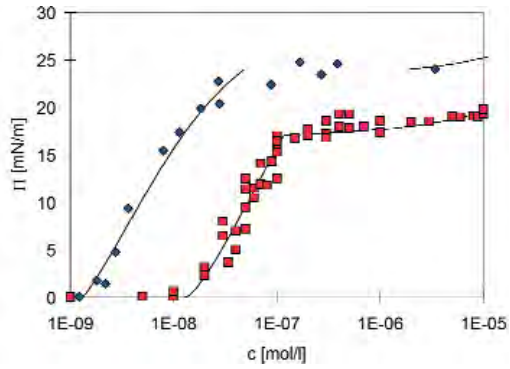

Fig. 2: Dependence of surface pressure Π on concentration c of β-casein (◆) and HSA (■), points are experimental data, curves calculated from the new model [1]

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

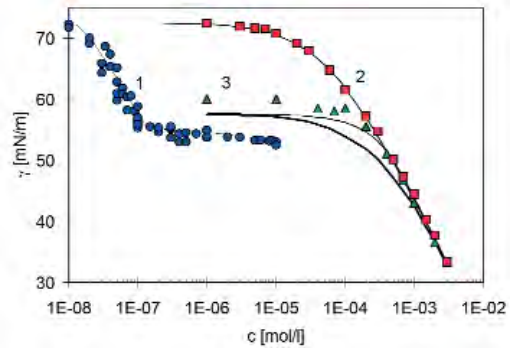

Fig. 3: Surface tension of HSA (●), C_{10}DMPO (■) and of mixed solutions of HSA (10^{-7}mol/l) with C_{10}DMPO (▲), points are experimental data from literature, curves calculated from the new model [2]

Adsorption Kinetics of Mixed Protein-Surfactant Adsorption Layers

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

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

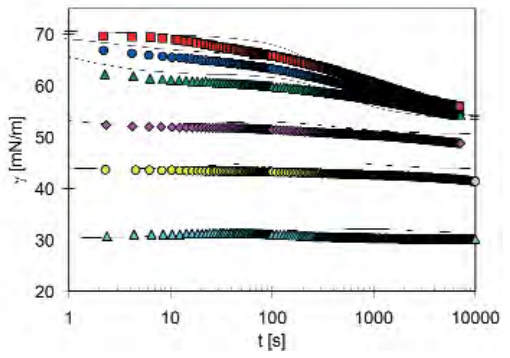

Fig. 4: Dynamic surface tension of a 10^{-6}mol/l β-LG solution mixed with C_{10}DMPO at different concentrations c = 0.01 (■); 0.04 (●); 0.1 (▲); 0.4 (◆); 1.0 (●); 4.0 (▲) mmol/l, points are experimental data from literature, curves calculated from the new model [2]

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

Dilational Rheology of Protein Adsorption Layers

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

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

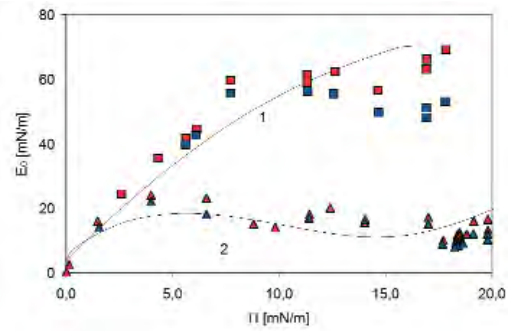

Fig. 5: Dependence of the limiting surface elasticity E_0 on the surface pressure, BSA (1) and β-casein (2), points are experiments for BSA at frequencies 0.084 (■) and 0.84 rad/s (■), and for β-casein at frequencies 0.033 (▲) and 0.84 rad/s (▲) [3]

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

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Key Publications:

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

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

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

Molecular Organization in Soluble Monolayers and Functional Films

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Aims

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

Results

Ion Distribution at Interfaces

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

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

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

Surface Rheology and Foam Stability

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

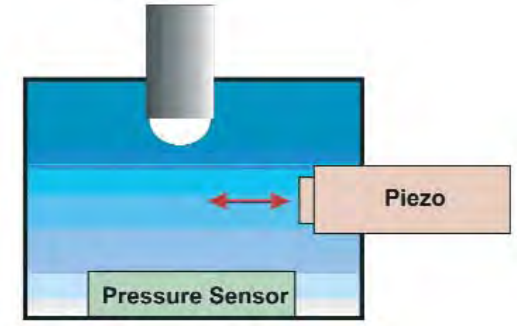

Fig. 1: Cross sectional view of the oscillating bubble device

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

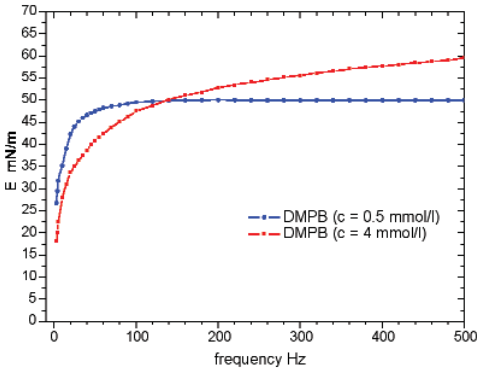

Fig. 2: Magnitude of the E-module for aqueous solution of DMPB

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

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

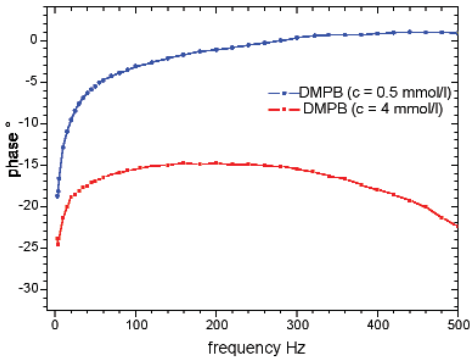

Fig. 3: Phase shift between piezo oscillation and measured pressure signal for aqueous solution of DMPB

Interfacial Water

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

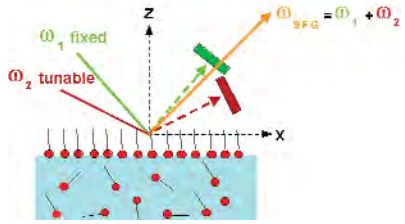

Fig. 4: Principle of IR-VIS sum frequency generation spectroscopy

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

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

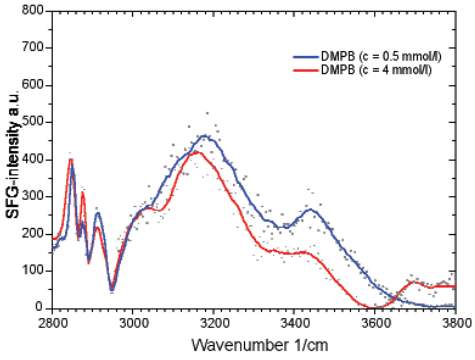

Fig.5: IR-VIS sum frequency spectra of DMPB of the interfacial water at two different surfactant concentrations

Surface Plasmon Spectroscopy

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

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Key Publications:

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

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

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

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

Rheological Properties of Fluid Interfaces

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Aims

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

Results

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

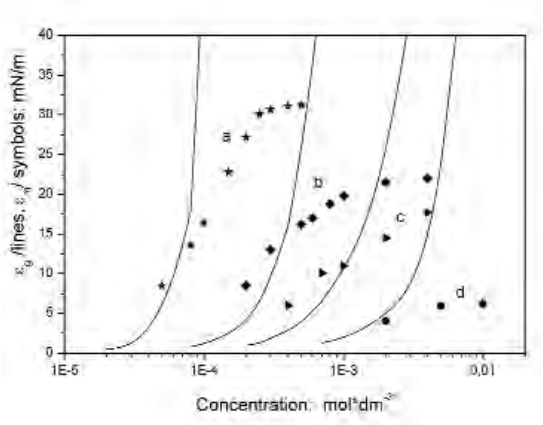

Fig. 1: Comparison between theoretical (line) and experimental Gibbs elasticities of n-nonanol (a), n-octanol (b), n-heptanol (c), and n-hexanol (d) solutions [1].

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

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

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

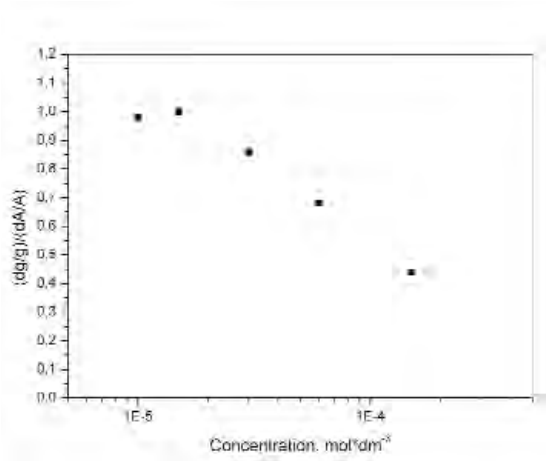

Fig. 2: The ratio of the relative change in surface concentration, dg/g, and the relative area change, dA/A, of a SGH-sensitive fluortenside solution during a fast bubble oscillation [2].

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

Further activities of the group were:

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

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Key Publications:

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

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

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

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

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1996: Habilitation (Mainz University)
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Aims

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

Our research focuses on the interaction/coupling between solid/liquid phase transitions and molecular transport (wetting, molecular flow, etc.). These processes are relevant for the early stages of solidification/melting (nucleation, cluster formation) as well as (non-equilibrium) bulk aggregation.

We specifically address the following topics/questions: What processes govern two-dimensional nucleation for different surface coverages and cooling rates? What is the relation between the interfacial alkane ordering and the statics and dynamics of wetting? Into which domain morphologies aggregate the interfacial molecules under various growth conditions?

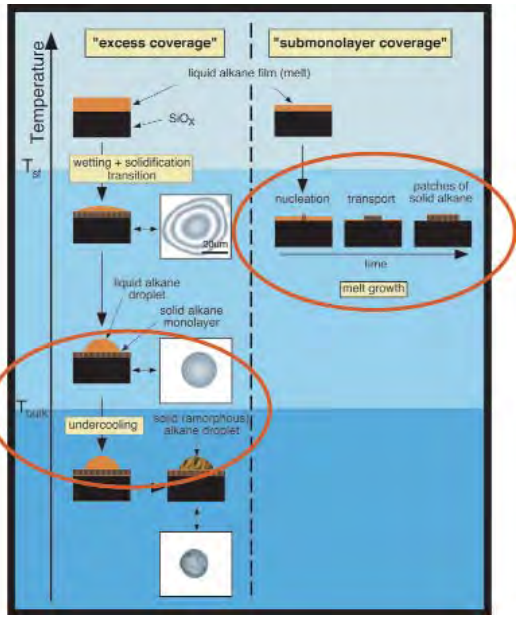

Fig. 1: Selection of topologies of alkanes at solid/gas interfaces (encircled are the regions of special interest to us).

Results

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

1.) In the high temperature range (light blue background) all alkane is molten and forms a completely wetting film of uniform thickness.
2.) In an intermediate range (medium blue), the alkanes adjacent to the solid surface solidify ("surface freezing"). If there is excess alkane ("excess coverage"), it remains liquid and shows a wetting transition at T_{sf} from a completely wetting film to droplets on top of the frozen layer.
3.) Below the bulk melting temperature, T_{bulk} (darker blue), all alkane is solid (in equilibrium).

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

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

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

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

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

For *sub-monolayer coverage*, upon solidification, the alkanes aggregate into domains with the molecules oriented upright at the interface in an alltrans conformation. **Fig. 2** shows an example of on-line observations of this nucleation-

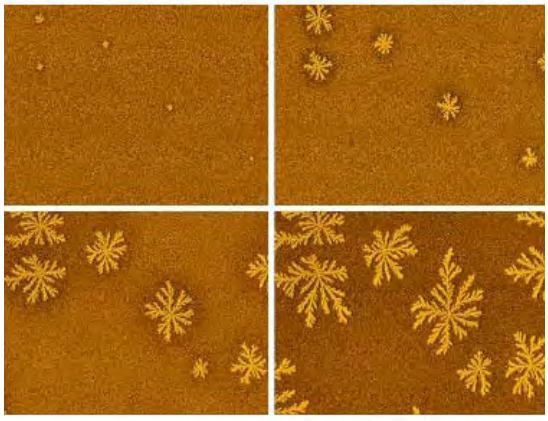

Fig. 2: Time sequence of microscopy frames showing a nucleation-dewetting-aggregation process. The bright fractal-shaped solid alkane domains are about 30Å thicker than the surrounding liquid alkane film (please note the depletion zone in front of the domains).

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

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

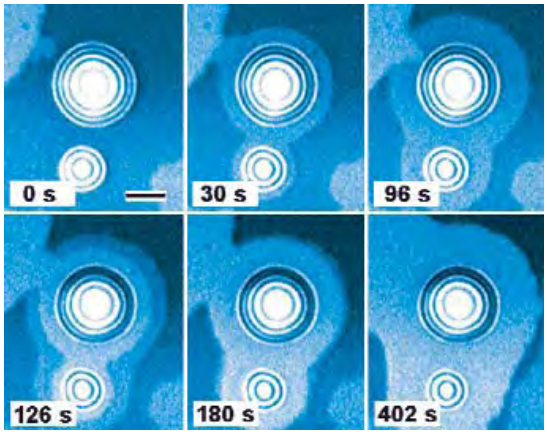

Fig. 3: Growth of solid mono/bi-layer terraces

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

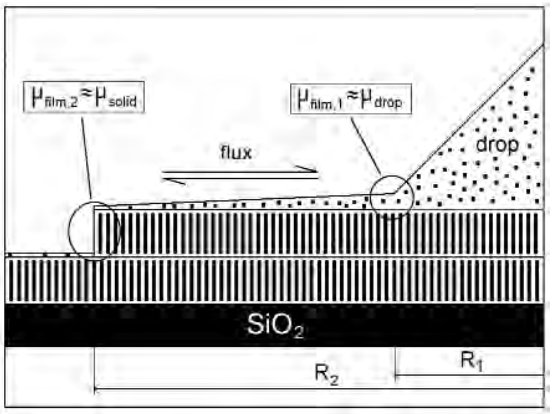

Fig. 4: Schematic of a cross-sectional cut through a growing monolayer terrace

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

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

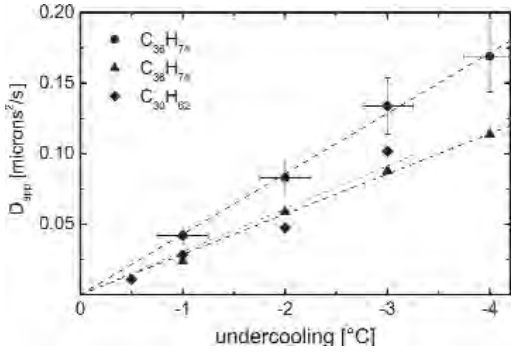

Fig. 5: Apparent diffusion constant as function of undercooling

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

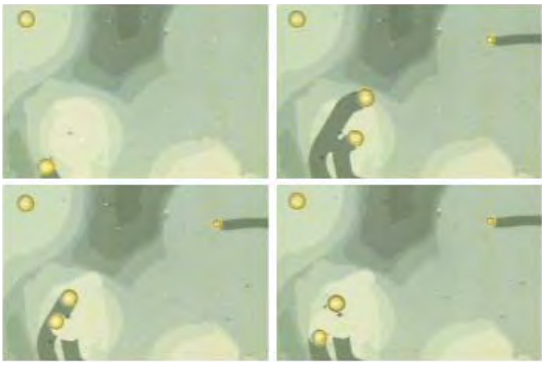

Fig. 6: Advancing (upper two frames, T>bulk melting) and receding (lower two frames, T<bulk melting) droplets

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Key Publications:

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

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

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

Nanoscale Membranes: Adhesion and Mechanics

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

Membranes with nanoscale thickness are abundant in nature, for example in form of the walls of cells, viruses or bacteria. These examples show impressively that membranes can be more than just static "barriers": Rather they can be sensitive towards external parameters like stress or chemical environment, adapt to their environment or carry out active processes like movement.

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

Results

Membrane Mechanics: Force Spectroscopy of Capsules and Flat Membranes

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

We have applied colloidal probe AFM in combination with optical techniques **[1]** for studying the force-deformation characteristics of individual (hollow) microcapsules and developed continuum and finite element analysis methods to derive elastic constants of the membrane materials from the measurements. The technique is suitable for a broad range of capsule systems and was so far used for studying the mechanical properties of polyelectrolyte multilayer capsules (PEC) and crosslinked pickering emulsion systems (CPE).

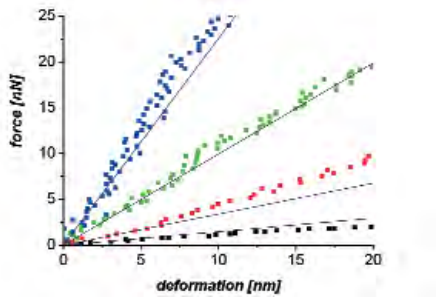

Fig. 1: Force versus deformation data for capsules of radius between 2 and 5 microns and wall thickness between 20 and 60 nm. Wall thickness and radius allow adjusting the capsule compliance over a large range, the solid lines are theoretical predictions based on continuum mechanics assuming a constant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

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

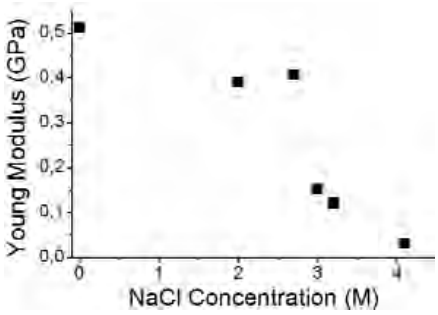

Fig. 2: Dependency of the Young modulus of polyelectrolyte capsules on the salt concentration derived from capsule deformability measurements.

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

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

Membrane Adhesion: From Basic Understanding to Patterning

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

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

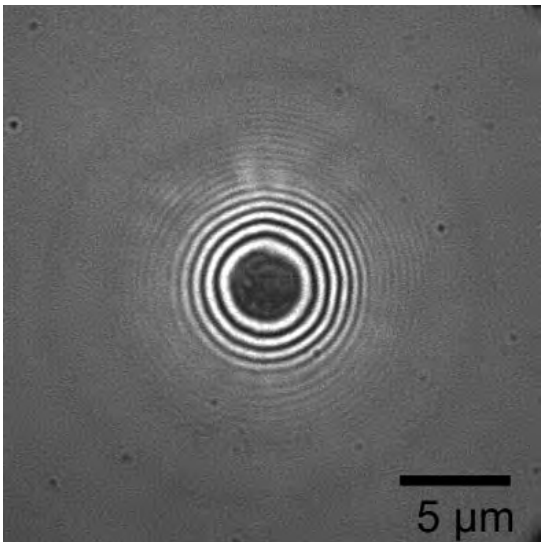

Fig. 3: RICM micrograph of an adhering capsule. The fringes correspond to the non contact regions close to the adhesion area (circular greyish area in the middle). The capsule shape can be reconstructed from the interferences.

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

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

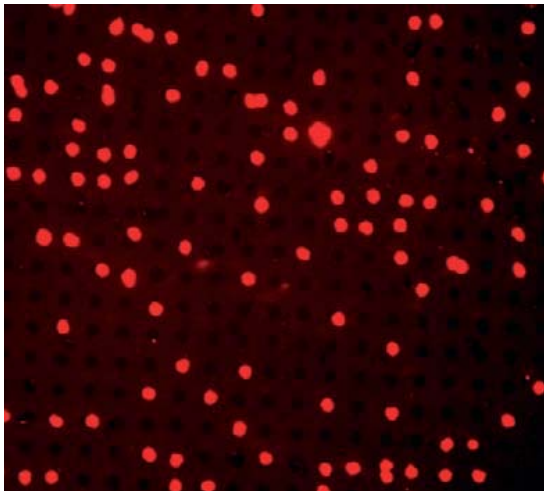

Fig. 4: Selective deposition of PECs on structured surfaces. The structure was printed with weakly labelled positively charged polyelectrolyte, while the positively charged PECs were strongly labelled; thus structure and shells are visible in the fluorescence image. The capsules are preferentially adsorbing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

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Key Publications:

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

Modular Materials: From Dynamic to Nanotechnological Devices

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Since 1996: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 1/2004: Adj. Professor (Potsdam University)
Since 4/2004: Director, Functional Modules Group (National Institute for Materials Science, Tsukuba, Japan)

Aims

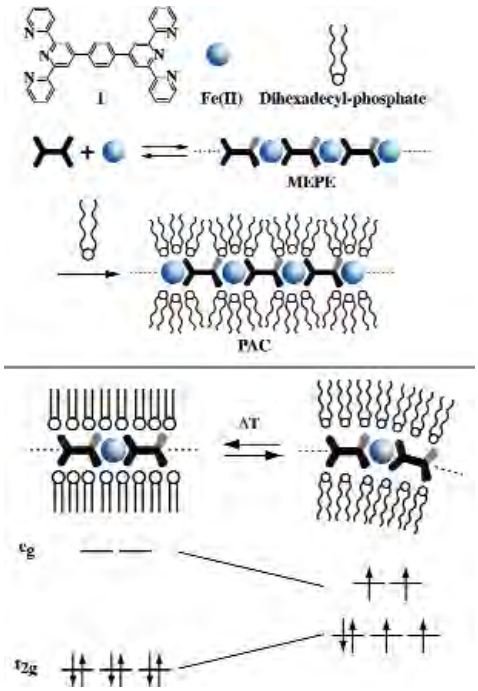
Metallo-supramolecular modules are at the focus of materials research for the construction of functional devices for sensing, transformation (catalysis), and signal transduction. The increasing importance of MEMOs rests on the fact that self-assembly of metal ions and ligands provides an elegant and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

Results

A. Metallo-Supramolecular Modules (MEMOs)

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

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



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

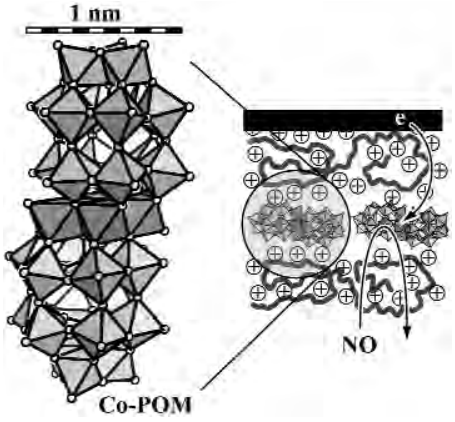
The occurrence of semi-occupied d-orbitals is responsible for some of the most prominent properties: The splitting of the d-orbitals in a ligand field of appropriate symmetry and strength can give rise to thermally or photo-induced spin transitions and spin crossover phenomena. The conversion between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

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

B. Polyoxometalate Clusters (POMs)

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

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



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

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

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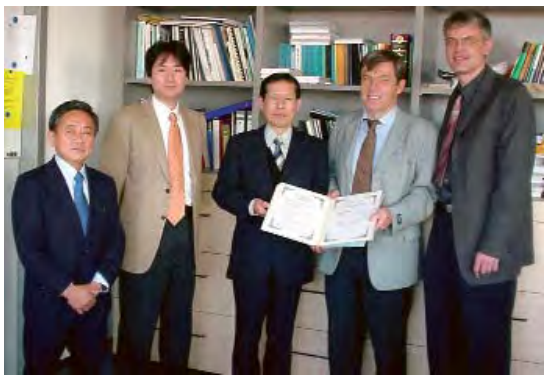
Functional Modules Group

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

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



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

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Key Publications:

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

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

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

Bioinspired Control of Electrical and Optical Properties of Interfaces

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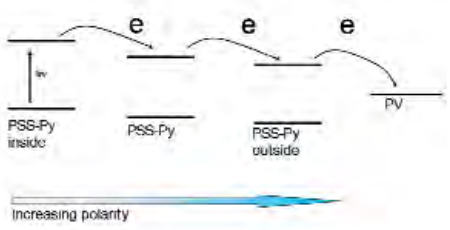
Aims

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

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



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

Results

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

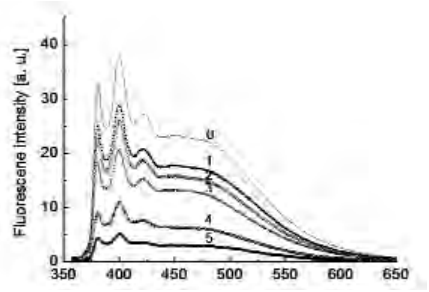


Fig.1a: Fluorescence spectrum of PSS-Py on adding increasing amounts (0-5) of the acceptor PV and for the film composition of Fig. 1b

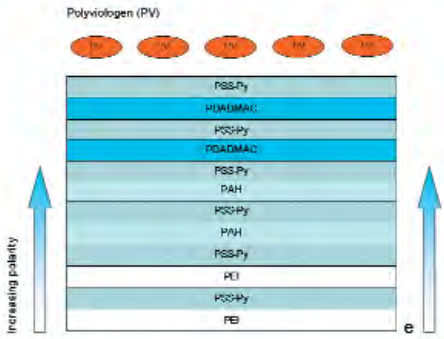


Fig.1b: Film design with PSS-Py in each anionic layer and with different polycations effecting a polarity gradient

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

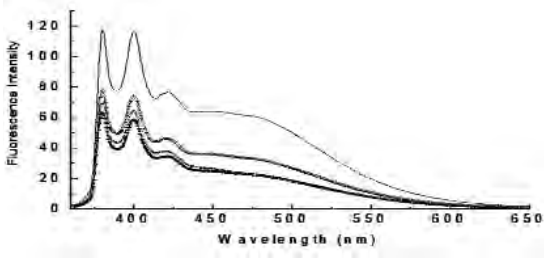


Fig. 2a: Fluorescence spectrum of PSS-Py with increasing acceptor concentration (top to bottom) for the film composition of Fig. 1b. Due to the insulating middle PSS layer the emission can not be decreased further by more PV addition

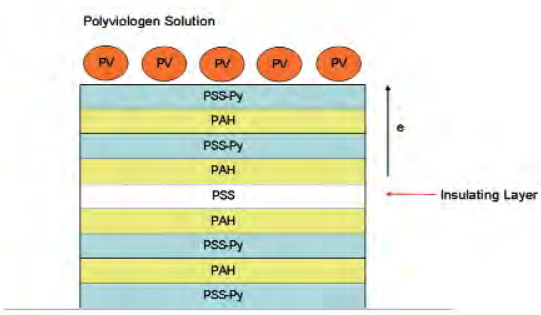


Fig. 2b: Film design with a middle PSS layer without Py coupled (insulating layer)

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

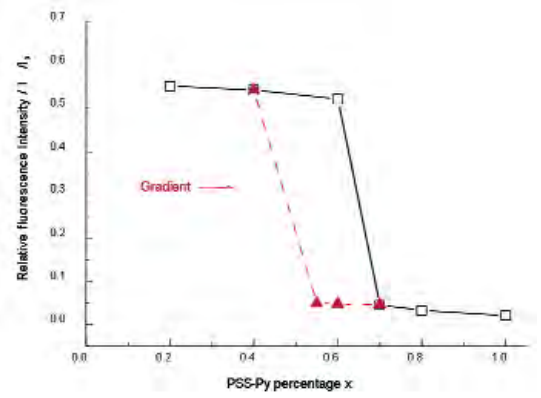


Fig. 3: Fluorescence intensity at maximum quenching (highest PV concentration) varying the PSS-Py/PSS ratio in the middle layer for the geometry of Fig. 2b (black squares) or for an analogous geometry but with a polarity gradient prepared as sketched in Fig. 1b (red triangles)

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

Future Work

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

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

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

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Key Publications:

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

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

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

Multifunctional Polyelectrolyte-based Micro- and Nanocapsules

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Aims

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

Results

Stimuli-Responsive Capsules as Microsensors and Microreactors:

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

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

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

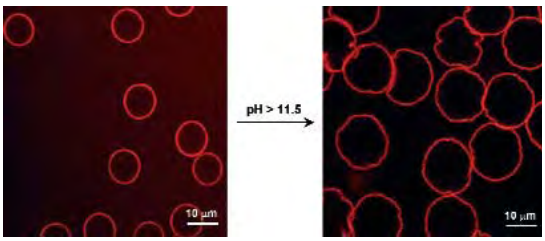

Fig. 1: Swelling of $(PAH/PSS)_n$ capsules in alkaline conditions

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

Polyelectrolyte Capsules as Protective Microcontainers:

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

Nanosynthesis in the Capsule Volume:

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

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

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

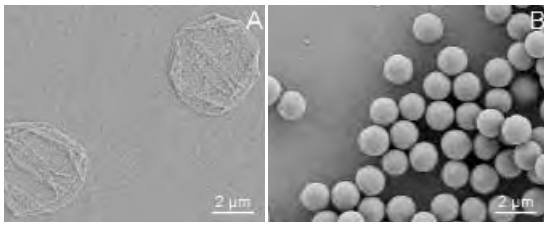

Fig. 2: Scanning electron microscopy images of dried $(PSS/PAH)_5$ polyelectrolyte capsules before (A) and after (B) incubation at 120 °C for 20 minutes

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

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

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

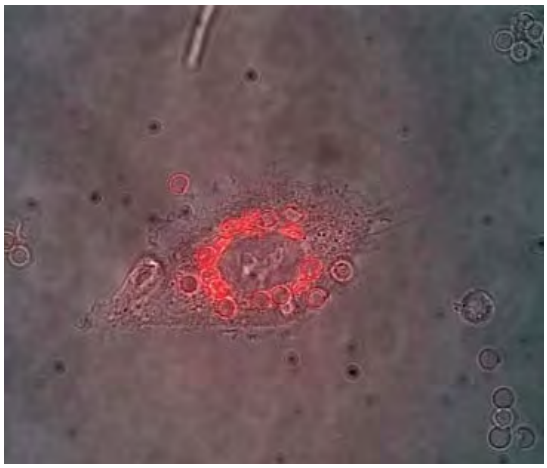

Fig. 3: Image of polyelectrolyte capsules fluorescently labelled with quantum dots after internalisation by breast cancer cells (in collaboration with LMU München – Dr. W. Parak, Dr. A. Rogach)

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

G. Sukhorukov, A. Antipov, M. Bédard, A. Cordeiro, C. Déjugnat, R. Georgieva, D. Gorin, A. Günther, D. Halozan, K. Köhler, O. Kreft, T. Mauser, A. Petrov, A. Praast, M. Prevot, I. Radtchenko, S. Sadasivan, D. Shchukin, D. Shenoy, A. Skirtach, D. Volodkin,
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Key Publications:
[1] Köhler, K., Shchukin, D.G., Sukhorukov, G.B., Möhwald, H.: Drastic Morphological Modification of Polyelectrolyte Microcapsules induced by High Temperature. Macromolecules **37**, 9546-9550 (2004).
[2] Mauser, T., Déjugnat, C., Sukhorukov, G.B.: Reversible pH-dependent properties of multilayer microcapsules made of weak polyelectrolytes. Macromol. Rapid Commun. **25**, 1781-1785 (2004).
[3] Sukhorukov, G.B., Volodkin, D.V., Gunther, A.M., Petrov, A.I., Shenoy, D.B., Möhwald, H.: Porous calcium carbonate microparticles as templates for encapsulation of bioactive compounds. J. Materials Chemistry, **14** (14), 2073-2081 (2004).
[4] Shchukin, D.G., Sukhorukov, G.B.: Nanoparticle Synthesis in Engineered Organic Nanoscale Reactors. Adv. Mater. **16**, 671-682 (2004).
[5] Skirtach, A.G., Antipov, A.A., Shchukin D.G., Sukhorukov G.B.: Remote activation of capsules containing Ag nanoparticles and IR dye by laser light. Langmuir **20**, 6988-6992 (2004).

Ordering of Functional Nanoparticles

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Aims

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

Results

A. Sub- or Microparticle Self-Assembly

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

(i) Binary Colloidal Crystals

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

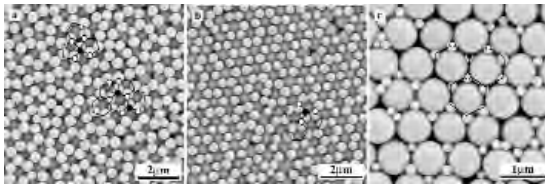

Fig. 1: SEM micrographs of the binary colloidal crystals produced by stepwise spin coating, in which small silica spheres were confined within the interstices between hexagonal close packed large ones.

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

(ii) Nanocrystal-Tagged Hydrogel Spheres

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

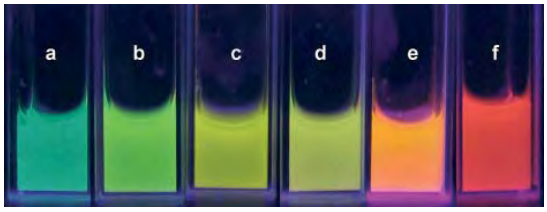

Fig. 2: Fluorescence images of hydrogel spheres incorporated with 2.5 nm (green) and 4 nm CdTe ones (red) and their mixtures with varied molar ratios.

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

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

(iii) Patterning Microsphere Surfaces

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

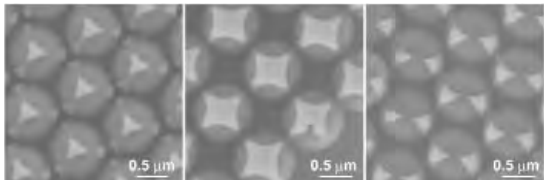

Fig. 3: SEM micrographs of polystyrene spheres with Au-patterned surfaces generated by templating the top monolayers of colloidal crystals with different crystal orientations.

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

B. Nanoparticle Self-Assembly

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

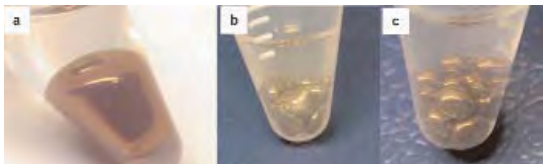

Fig. 4: Photographs of water droplets enclosed by thin films of Au (a) and Ag nanoparticles (a) and of their mixture, formed at the water/toluene interface.

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

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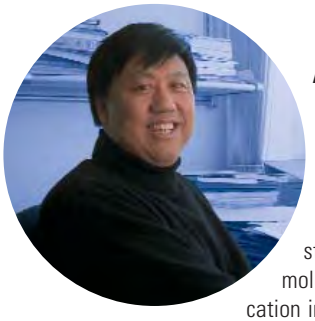
Key Publications:

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

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

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

Molecular Assembly of Biomimetic Systems



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1993-1996: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
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Aims

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

Results

Biomolecular Recognition and Membrane Hydrolysis

The hydrolysis reaction of phospholipid monolayers at the air/water interfaces catalyzed by different enzymes, like PLA_2, PLD, PLC has been deeply studied by means of newly developed spectroscopic and microscopic techniques so that the mechanism of interfacial hydrolysis can be better understood. The morphological changes of lipid monolayers caused by the adsorption of enzymes, and the quantitative analysis of hydrolysis products are investigated. **(Fig. 1)**

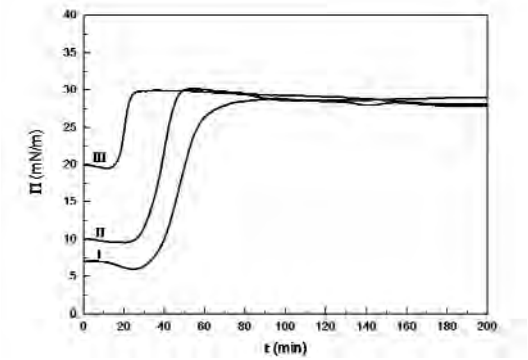
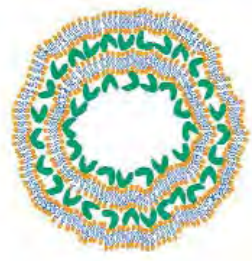


Fig. 1: Curves of surface pressure p as a function of time t of L-DPPC monolayer after the injection of PLC into the subphase at different initial pressures. C PLC = 10 units

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

Biogenic Microcapsules

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



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

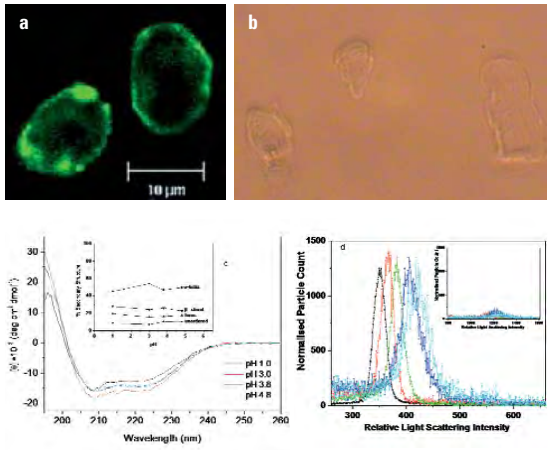


Fig. 2: (a) Fluorescence microscopic image of (HSA/DMPA)4 encapsulated ibuprofen crystals. 5% NBD-DMPC was used as fluorescent label. (b) Intact hollow capsules after the release of Ibuprofen crystals. (c) CD spectra of HSA at different pH values. (d) Single particle light scattering experiment confirms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

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

size. The enzymatic reaction occurring at the surface alters the permeability of the capsule, which may lend the capsule new features. This procedure can be applied for biomimetic cells to study reactions in a living system.

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

Fabrication of Nano Structured Biomaterials

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

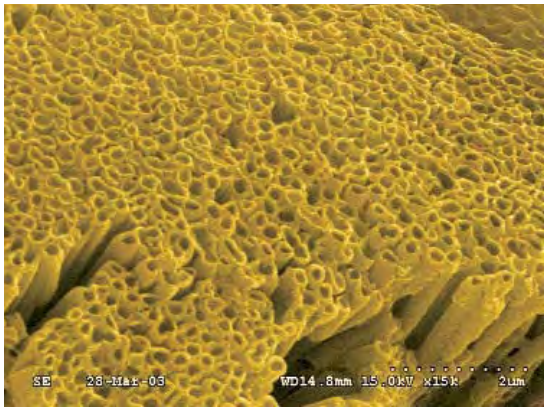


Fig. 3: Scanning electron micrographs of DMPA/HSA nanotubes obtained by template-based self-assembly

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

Selective Control of Cell Adhesion on Patterned Substrates

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

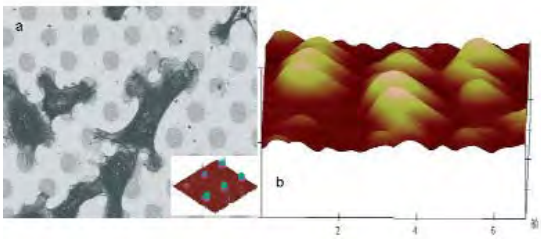


Fig. 4: Immobilizations of (a) RGD on patterned NIPAM polymer brushes and (b) liposomes on supported lipid bilayer patters.

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

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Collaborated with MPI: G. Brezesinski, H. Möhwald.
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Key Publications:

[1] Ge, L.Q., Möhwald H., Li, J. B.: Phospholipase A2 hydrolysis of mixed phospholipid vesicles formed on polyelectrolyte hollow capsules. Chem. Eur. J. **9**, 2589-2594 (2003).

[2] Ai, S. F., Lu, G., He, Q., Li, J. B.: Highly flexible polyelectrolyte Nanotubes. J. Am. Chem. Soc. **125-37**, 11140-11141 (2003).

[3] An, Z. H., Lu, G., Möhwald, H., Li, J. B.: Self-assembly of human serum albumin (HSA) and L-a-dimyristoylphosphatitic acid (DMPA) microcapsules for controlled drug release. Chem. Eur. J. **10**, 5848-5852 (2004).

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

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1996: Diploma, Polymer Chemistry (University Pierre et Marie Curie, Paris, France)
Thesis: Anionic polymerization of phenyl glycidyl ether in miniemulsion
2000: PhD, Polymer Chemistry (University Montpellier II, France)
Thesis: Controlled/living radical polymerization in the presence of β-phosphonylated nitroxides
2001-2003: Postdoc (Carnegie Mellon University, USA)
Since 2003: Group Leader (Fraunhofer Institute for Applied Polymer Research, Potsdam)

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

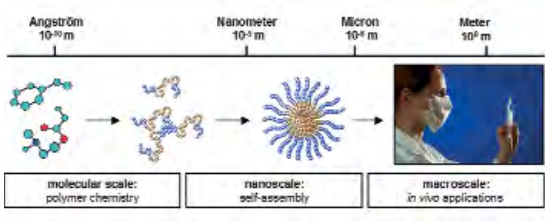

Fig. 1: Strategy for preparing tailored nanostructures for life-science applications

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

Our first objective is to prepare at the molecular level well-defined macromolecules with a life science potential, such as water soluble polymers, amphiphilic copolymers, hybrids of synthetic polymers and biomacromolecules, biodegradable polymers, polymer bioconjugates, stimuli responsive polymers… For reaching this goal, we are using and combining several modern methods of synthesis such as controlled radical polymerization **[1,2]**, living polymerization of polypeptides **[3]**, ring opening polymerization or click chemistry **[4]**. All these methods constitute an original "macromolecular toolbox", which permit to synthesize macromolecules with a tailor-made molecular structure (i.e. controlled chain-length, molecular weight distribution, composition, architecture and functionality). A good example of our synthetic work is the preparation via radical polymerization of synthetic polymers and copolymers bearing nucleic acids moieties such as thymine, adenine or uracil **[5]**. These original polymers were prepared using controlled radical polymerization techniques and possess a good potential for interacting with natural biomacromolecules such as DNA or proteins and therefore can be used in bioseparation devices. The properties of such macromolecules are currently under investigation in a cooperation project with Andreas Thünemann at the Bundesanstalt für Materialforschung und -prüfung (BAM, Berlin).

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

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

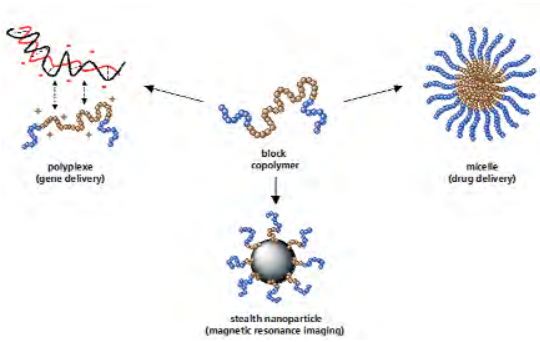

Fig. 2: Various nanostructures obtainable via the self-asembly of segmented copolymers

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

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

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

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Key Publications:

[1] Lutz, J.-F., Neugebauer, D., Matyjaszewski, K.: Stereoblock copolymers and tacticity control in controlled/living radical polymerization. J. Am. Chem. Soc. **125**, 6986-6993 (2003).
[2] Lutz, J.-F., Jahed, N., Matyjaszewski, K.: Preparation and characterization of graft terpolymers with controlled molecular structure. J. Polym. Sci., Part A: Polym. Chem. **42**, 1939-1952 (2004).
[3] Lutz, J.-F., Schütt, D., Kubowicz, S.: Preparation of Well-Defined Diblock Copolymers with Short Polypeptide Segments via Polymerizations of N-Carboxyanhydrides. Macromol. Rapid Commun. **26**, 23-28 (2005).
[4] Lutz, J.-F., Börner, H.G., Weichenhan, K.: Combining ATRP and Click Chemistry: a Versatile Method for Preparing End-Functional Polymers. Macromol. Rapid Commun. (in press).
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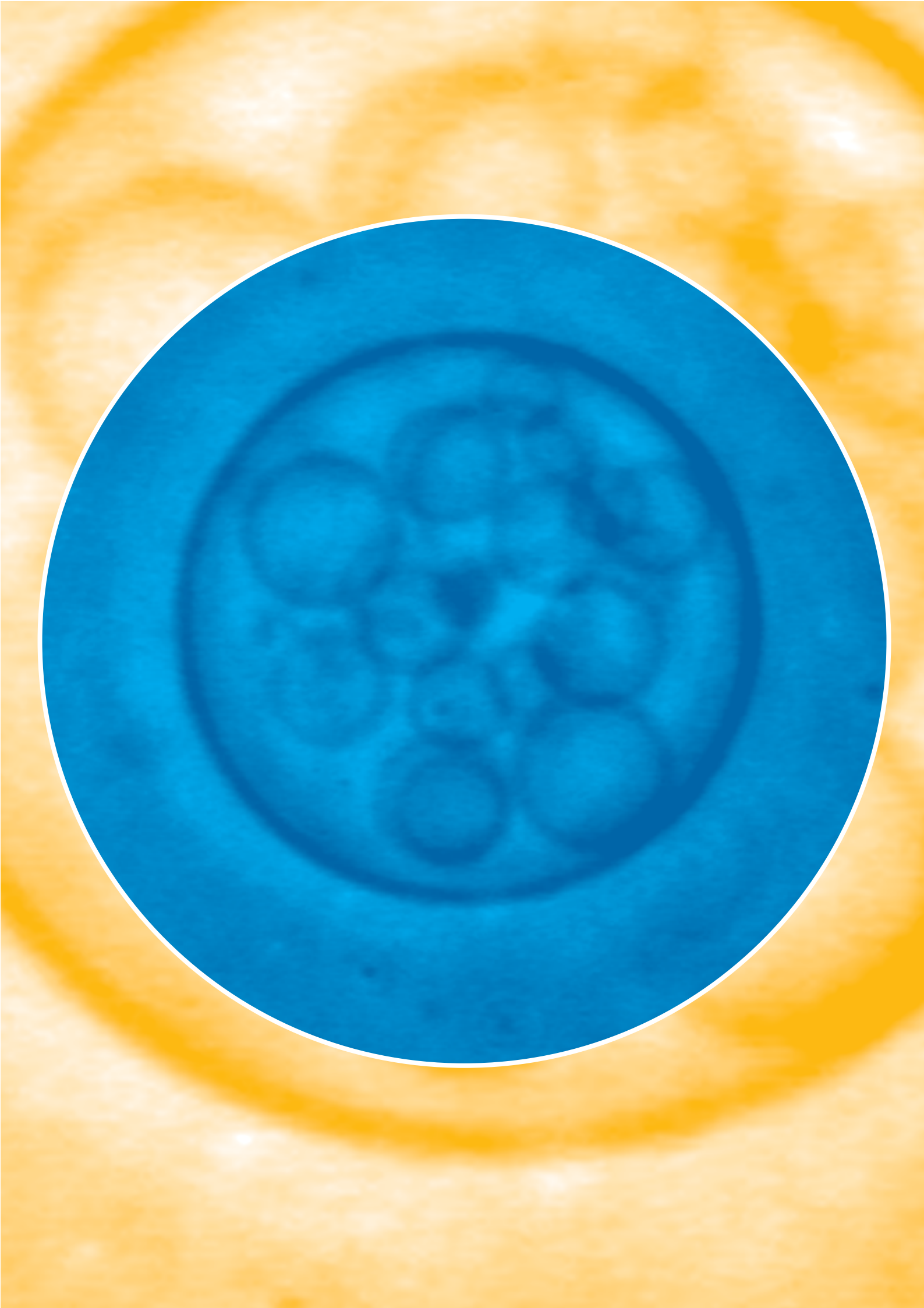
[6] Lutz, J.-F., Laschewsky, A.: Multicompartment Micelles: Did the Long-Standing Dream Become a Reality? Macromol. Chem. Phys. (in press).
[7] Kubowicz, S., Baussard, J.-F., Lutz, J.-F., Thünemann, A.F., v. Berlepsch, H., Laschewsky, A.: Observation of Multicompartment Micelles Formed via Self-Assembly of Linear ABC Triblock Copolymers in Aqueous Medium. Angew. Chem. Int. Ed., (submitted).
[8] Rocha, S., Brezesinski, G., Möhwald, H., Thünemann, A.F.: Secondary Structure of the Fusogenic Peptide B18 in the Presence of Nanoparticles. ChemBioChem **6**, 1-4 (2005).

THEORY



Research in the Theory Department

Es gibt nichts Praktischeres als eine gute Theorie
Immanuel Kant

Structure of the Theory Department

The researchers and doctoral students of the Theory Department form one experimental and seven theoretical research teams. Each of these teams consists of the team leader and several students. The team leaders are:

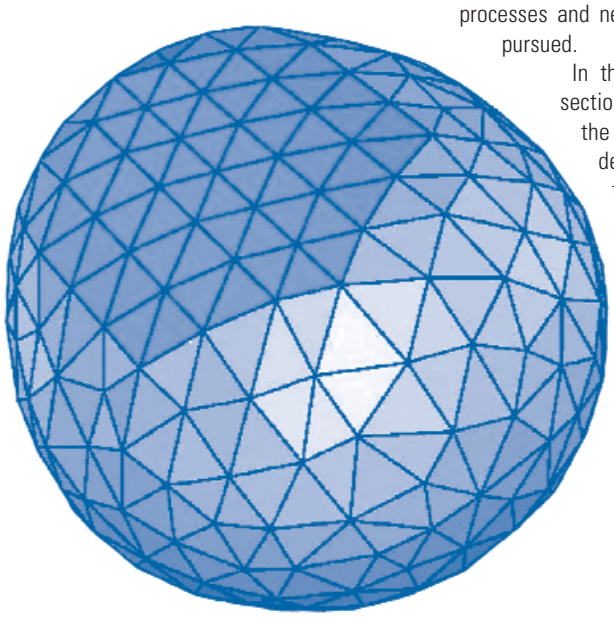
- Rumiana Dimova (experiment, membranes and vesicles).
- Thomas Gruhn (theory, membranes and vesicles);
- Jan Kierfeld (theory, polymers and filaments);
- Stefan Klumpp (theory, transport by molecular motors);
- Ulrich Schwarz (theory, membranes and cells) (until 2005);
- Christian Seidel (theory, polymers and polyelectrolytes);
- Julian Shillcock (theory, supramolecular modelling);
- Thomas Weikl (theory, proteins and membranes).

The Theory Department is responsible for the International Max Planck Research School and for the European Early Stage Training Network in which three departments of the MPI participate. The management of these networks is done by Angelo Valleriani.

Research in the Theory Department is focused on fundamental aspects of colloids and interfaces. In most cases, we study biomimetic model systems which are inspired by the nanostructures found in biological systems. Two examples are bilayer membranes with several components and active transport by molecular motors. In addition, some work has been done to directly address the complexity of biological systems. Two examples are the kinetics of protein folding and the elastic interactions of cells.

The conceptual framework for the understanding of these systems and their cooperative behavior is provided by *statistical physics* which includes thermodynamics, statistical mechanics, and stochastic processes. Some fundamental aspects of statistical physics such as irreversible processes and networks have also been pursued.

In the following three subsections, the research within the Theory Department is described in more detail in terms of the underlying systems which exhibit a hierarchy of structural levels, the generic phenomena found in these systems, and the methods used to study them.



Systems

First, one can emphasize the various systems which are studied in the department. If one looks at these systems bottom-up, i.e., from small to large scales, one can distinguish several levels of bionano systems as shown in **Fig. 1**.

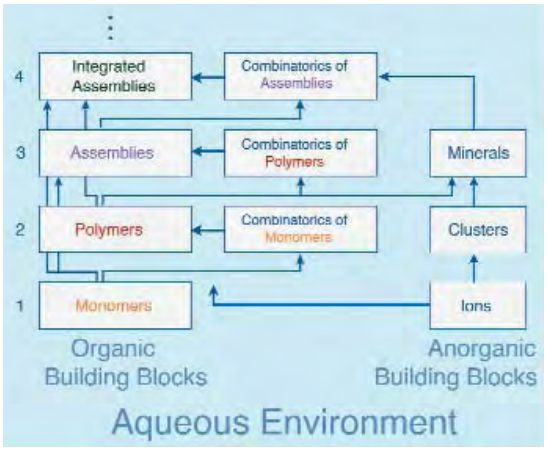


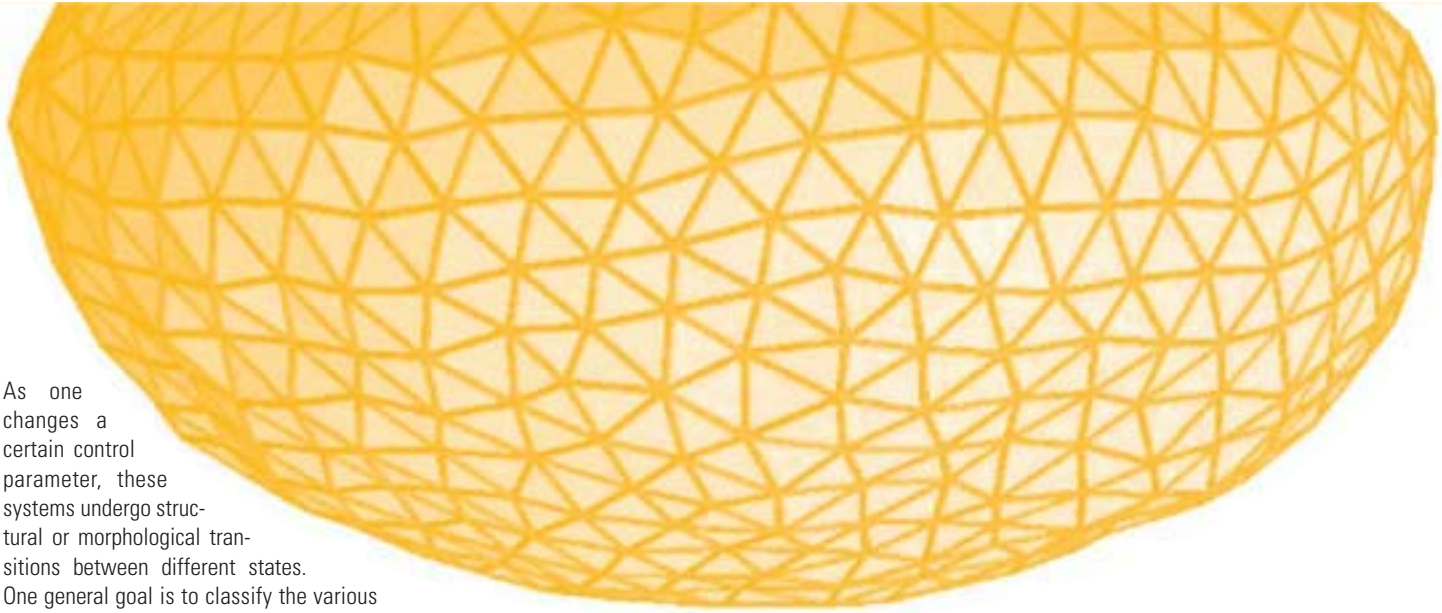
Fig. 1: Hierarchy of bionano systems, i.e., of biological and biomimetic systems in the colloidal regime between nanometers and micrometers. The assembly pathway on the left proceeds from small molecules or monomers to integrated assemblies, i.e., to 'assemblies of assemblies' that may differ in their architecture. The assembly pathway on the right leads to small mineral particles that are stabilized by adsorbed polymers.

During the last two years, research on biomimetic systems has been focussed on the levels of polymers (polyelectrolytes, semi-flexible polymers, mesoscopic rods), assemblies (cytoskeletal filaments, bilayer membranes), and integrated assemblies consisting, e.g., of filaments, motors, and cargo particles such as vesicles. Research on biological systems addressed the level of polymers in the context of protein folding and the level of whole cells which lies above those shown in **Fig. 1**.

If one looks at these systems top-down, i.e., from large to small scales, one encounters the problem of restricted geometries or confining walls and interfaces. One topic in this latter research area which has been studied in some detail were liquids at chemically and topographically structured surfaces.

Phenomena

At each level shown in **Fig. 1**, one encounters a variety of cooperative phenomena. These systems contain flexible or soft components that undergo thermally excited fluctuations corresponding to cooperative Brownian motion because the ambient temperature corresponds to liquid water. One would like to determine both, the typical states or morphologies attained by these systems and their fluctuation spectrum. In addition, these fluctuations lead to entropically induced forces which compete with the direct molecular forces.



As one changes a certain control parameter, these systems undergo structural or morphological transitions between different states. One general goal is to classify the various possible states and their transitions. This classification leads to "state", "morphology", or "phase" diagrams which describe the system's behavior in a global manner.

One structural transition which has been studied in the Theory Department during the last two years, both experimentally and theoretically, is the fusion of bilayer membranes and vesicles. In the experiments, the fusion was induced by the addition of multivalent ions which act to crosslink certain membrane-anchored molecules. In the simulations, the fusion was controlled by the initial tensions within the membranes. At present, the length scales accessible to experiments and simulations are still rather different whereas the time scales now begin to have some overlap.

Membrane fusion starts from an adhering state and is completed when the fusion pore has been formed. Such a fusion event represents an irreversible relaxation or "down-hill" process that proceeds from an initial state out of equilibrium towards another more stable state.
In order to reverse this process, one would need to involve a molecular motor that can break the neck of the fusion pore again. Such a motor must be able to couple the fission of the fusion pore, which represents an endergonic "uphill" process, to another process that represents an exergonic "down-hill" process. This type of coupling provides the basic mechanism for all active processes in biological systems.

Active biomimetic processes have now become a main focus of the Theory Department.

One important example is the transport by molecular motors. In this context, we have studied a variety of cooperative motor phenomena: build-up of traffic jams of motors; active structure formation leading to steady states with spatially non-uniform density and current patterns; and active phase transitions between different steady states far from equilibrium. A particularly simple active phase transition with spontaneous symmetry breaking is predicted to occur in systems with two species of motor particles which walk on the filaments in opposite directions.

Current projects on active processes include: effect of disordered filaments and regulatory proteins on motor transport; active force generation by polymerization; cooperative behavior of filaments on motor covered substrates; adhesion of membranes with active stickers.

In addition, the Theory Department coordinates a new European network (STREP) on "Active Biomimetic Systems".

Methods

The theoretical work starts with the definition of a certain model which (i) is amenable to systematic theoretical analysis and (ii) captures the essential features of the real system and its behavior. New models which have been introduced in the Theory Department include: semi-flexible harmonic chains for filaments; coarse-grained molecular models for bilayer membranes; lattice models for membranes with adhesion molecules; geometric models for membranes with lateral domains; and lattice models for transport by molecular motors.

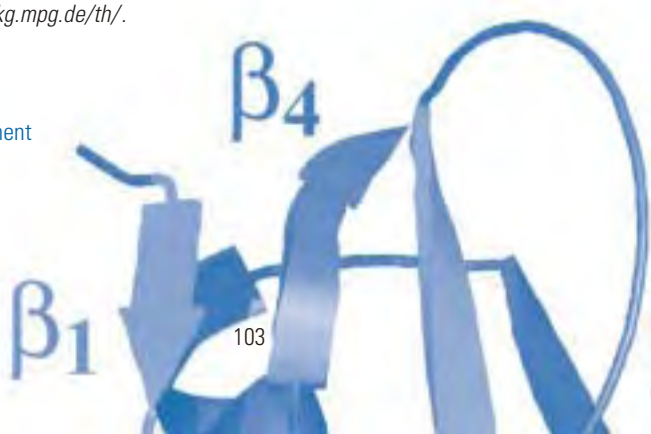
These theoretical models are then studied using the analytical tools of theoretical physics and a variety of numerical algorithms. The analytical tools include dimensional analysis, scaling arguments, molecular field or self-consistent theories, perturbation theories, and field-theoretic methods such as renormalization. The numerical methods include the application of mathematical software packages such as Mathematica or Maple as well as special algorithms such as, e.g., the Surface Evolver for the calculation of constant mean curvature surfaces.

Three types of computer simulations are applied and further developed: Molecular Dynamics, Dissipative Particle Dynamics, and Monte Carlo methods. Molecular Dynamics is applied to particle based models of supramolecular assemblies; Dissipative Particle Dynamics, which is a relatively new simulation algorithm, is useful in order to extend the Molecular Dynamics Studies towards much larger systems and longer time scales; Monte Carlo methods are used in order to simulate even larger mesoscopic systems such as filaments and membranes up to a linear size of hundreds of nanometers.

The experimental work is carried out in our membrane lab which is equipped with calorimetry, optical microscopy, micropipettes, and optical tweezers. An advanced confocal microscope is currently installed that will be available to all four departments of the MPI.

Additional information about research in the Theory Department is avalaible at *www.mpikg.mpg.de/th/*.

Reinhard Lipowsky
Director of the Theory Department



Wetting Morphologies at Structured Surfaces

Reinhard Lipowsky 11.11.1953
1978: Diploma, Physics,
Thesis with Heinz Horner on turbulence (University of Heidelberg)
1982: PhD (Dr. rer. nat.), Physics (University of Munich)
Thesis with Herbert Wagner on surface phase transitions
1979-1984: Teaching Associate with Herbert Wagner (University of Munich)
1984-1986: Research Associate with Michael E. Fisher (Cornell University)
1986-1988: Research Associate with Heiner Müller-Krumbhaar (FZ Jülich)
1987: Habilitation, Theoretical Physics (University of Munich)
Thesis: Critical behavior of interfaces: Wetting, surface melting and related phenomena
1989-1990: Associate Professorship (University of Munich)
1990-1993: Full Professorship (University of Cologne), Director of the Division "Theory II" (FZ Jülich)
Since Nov 1993: Director (Max Planck Institute of Colloids and Interfaces, Potsdam)

Many experimental methods have been developed by which one can prepare chemically and/or topographically structured substrates. If one deposits a certain amount of liquid on such a substrate, one experimentally observes a large variety of wetting morphologies.

Some years ago, we started to classify the possible morphologies at *chemically* structured surfaces theoretically. We discovered that these surfaces lead to *morphological wetting transitions* at which the wetting layer changes its shape in a characteristic and typically abrupt manner **[1, 2]**. We extended this work (i) to liquid channels or filaments with freely moving endcaps which leads to a morphology diagram with a line of discontinuous transitions that ends in a critical point **[3]**, see biannual report 2002+2003, (ii) to nucleation at circular surface domains which is characterized by an activation free energy with two maxima **[4]**, (iii) to vesicle adhesion at striped surface domains **[5]**, and (iv) to a general stability analysis of these morphologies **[6]**.

In the context of nonplanar substrates, we first studied chemically heterogeneous and *topographically* rough surfaces for which we derived the general functional relationship between contact angle, interfacial tensions, and line tension **[7]**. More recently, we considered topographically structured surfaces which contain surface channels (or grooves) and obtained a complete classification for the corresponding wetting morphologies **[8]**. The following contribution will focus on this latter work.

Open Systems for Micro- and Nanofluidics

An obvious prerequisite for "labs-on-a-chip" miniaturized labs are appropriate micro-compartments for the confinement of very small amounts of liquids and chemical reagents. Like the test-tubes in macroscopic laboratories, these micro-compartments should have some basic properties: They should have a well-defined geometry by which one can measure the precise amount of liquid contained in them; they should be able to confine *variable* amounts of liquid; and they should be accessible in such a way that one can add and extract liquid in a convenient manner.

An appealing design principle for such microcompartments is based on open and, thus, directly accessible surface channels which can be fabricated on solid substrates using available photolithographic methods. The simplest channel geometry that can be produced in this way corresponds to channels with a rectangular cross section. The width and depth of these channels can be varied between a hundred nanometers and a couple of micrometers.

Classification of Wetting Morphologies

As shown in our recent study **[8]**, liquids at surface channels can attain a large variety of different wetting morphologies including localized droplets, extended filaments, and thin wedges at the lower channel corners. Examples for these morphologies as observed by atomic (or scanning) force microscopy (AFM) are shown in **Fig. 1**.

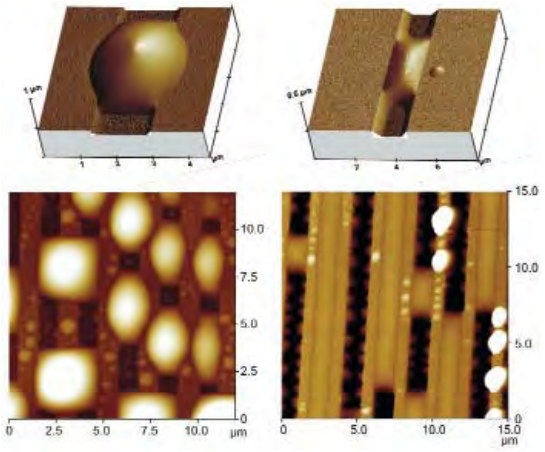


Fig. 1: Atomic (or scanning) force microscopy images of liquid morphologies on silicon substrates with rectangular surface channels which have a width of about one micrometer. On the left, the liquid does not enter the channels but forms large lemon-shaped droplets overlying the channels (dark stripes). On the right, the liquid enters the channels and forms extended filaments separated by essentially empty channel segments (dark stripes).In the bottom row, one sees several parallel surface channels in both images; in the top row, there is only one such channel with a single droplet (left) or filament (right). Close inspection of the upper right image reveals (i) that this filament is connected to thin wedges along the lower channel corners and (ii) that the contact line bounding the meniscus of the filament is pinned to the upper channel edges.

When the AFM experiments were first performed, it was not known how to produce a certain liquid morphology since there was no systematic theory for the dependence of this morphology on the materials properties and on the channel design. Such a theory has now been developed. Our theory addresses the strong capillary forces between substrate material and liquid and takes the 'freedom' of contact angles at pinned contact lines into account. Such a contact line is visible in the upper right image in **Fig. 1**. For this contact line, which is pinned along the channel edges, the contact angle θ_p is not determined by the classical Young equation but can vary over the range

$$\theta \le \theta_p \le \theta + \pi/2 \qquad (1)$$

for a surface channel with rectangular cross section where θ denotes the contact angle on all planar segments of the substrate surface (taken to be chemically homogeneous). An analogous 'freedom' is also found for those contact lines that are pinned to the boundaries of chemically defined surface domains as first emphasized and explored in our previous work **[1]**.

The classification described in **[8]** is based (i) on general considerations such as the relation given by (1), (ii) on analytical shape calculations which are feasible for relatively simple morphologies such as liquid filaments with constant cross section, see **Fig. 2**, and (iii) on numerical minimization of the liquid's free energy which leads to constant mean curvature surfaces. A surprising prediction of our theory is that the experimentally observed polymorphism of the wetting liquid

depends only on two parameters: (i) the aspect ratio X of the channel geometry, i.e., the ratio of the channel depth to the channel width; and (ii) the contact angle θ which characterizes the interaction between substrate material and liquid.

The corresponding morphology diagram, which is displayed in **Fig. 3**, represents a complete classification of all possible wetting morphologies.

Inspection of this figure shows that one has to distinguish seven different liquid morphologies which involve localized droplets (D), extended filaments (F), and thin wedges (W) at the lower channel corners.

For microfluidics applications, the most important morphology regime is (F^-) which corresponds to stable filaments. Since this regime covers a relatively small region of the morphology diagram, see **Fig. 3**, it can only be obtained if one carefully matches the channel geometry described by its aspect ratio *X* with the substrate wettability as described by the contact angle θ.

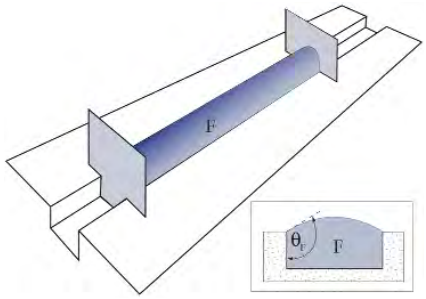


Fig. 2: Liquid filament (F^+) with positive Laplace pressure, i.e., with a meniscus that is curved upwards away from the substrate. The filament is located within the rectangular surface channel and is "sandwiched" between two pistons which provide walls orthogonal to the long axis of the filament. The contact angle at these walls is $\pi/2$ which ensures that the filament has constant cross-section and is bounded by a cylindrical meniscus. In mechanical equilibrium, the total force exerted by the filament onto each piston must vanish. The inset shows the filament cross section and the associated filament angle $\theta_p = \theta_F$ which is uniquely determined by the aspect ratio X of the surface channel and the contact angle θ of the substrate material.

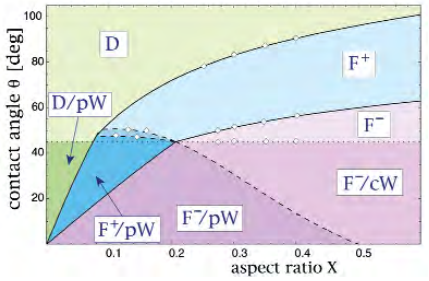


Fig. 3: Morphology diagram as a function of the aspect ratio X of the channel and the contact angle θ which characterizes the interaction between substrate material and liquid. This diagram contains seven different morphology regimes which involve localized droplets (D), extended filaments (F), and thin wedges (W) in the lower channel corners. The diagram represents a complete classification of all possible wetting morphologies and should be universal, i.e., should apply to other liquids and substrate materials as well.

Perspectives

One relatively simple application of the morphology diagram shown in **Fig. 3** is obtained if the system is designed in such a way that one can vary or switch the contact angle in a controlled fashion. One such method is provided by electrowetting; alternative methods, which have been recently developed, are substrate surfaces covered by molecular monolayers that can be switched by light, temperature, or electric potential. If one varies the contact angle by one of these methods, the system moves in the morphology diagram parallel to the vertical axis. It can then cross the boundary between the two morphology regimes (F^-) and (F^+). This transition leads to a controlled variation in the length of the liquid filament: these filaments enter the surface channels with decreasing contact angle but recede from these channels with increasing contact angle as has been demonstrated by electrowetting experiments.

The theory underlying the morphology diagram in **Fig. 3** predicts that this diagram is rather universal and applies to many different systems. The experiments described in **[8]** use a polymeric liquid that freezes quickly and can then be scanned directly with the tip of an atomic force microsope.

The morphology diagram should also apply to other liquids and other substrate materials. It should also remain valid if one further shrinks the surface channels and, in this way, moves deeper into the nanoregime. As one reaches a channel width of about 30 nanometer, one theoretically expects new effects arising from the line tension of the contact line, but such nanochannels remain to be studied experimentally.

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Mesoscopic Simulations of Complex Nanostructures and Processes

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The traditional boundaries between the scientific disciplines of Physics, Chemistry and Biology are being rapidly eroded at the nanoscale. This is a new development largely because at the macroscale it is clear that there is a vast difference between whole organisms, even ones as small as an amoeba, and the atoms and molecules of chemistry and physics. As one probes down to smaller length scales, however, these distinctions become increasingly artificial. Progress in electron microscopy, fluorescence techniques and micromanipulation have pushed the experimental resolution of investigations of the protein and lipid components of cells to smaller and smaller length scales while, simultaneously, novel computer simulation techniques are starting to reveal structure above the 50 nm and 100 ns marks. However, the intermediate region, between 100 nm and 1 micron, and 100 ns and 100 microseconds, is still partially obscure: the so-called twilight zone **[1]**.

In this project, we are using a mesoscopic simulation technique, Dissipative Particle Dynamics (DPD), to probe this twilight zone. We hope to predict the properties of "smart" self-assembled materials, such as amphiphilic membranes and actin filaments, from a knowledge of their constituents (see **Fig. 1**); and to reveal details of biophysical processes, such as vesicle fusion, unobtainable from continuum theoretical models and difficult to quantify from experiment. In collaboration with a group at University of Pennsylvania, we have also started to perform a systematic comparison of DPD simulations with more traditional Molecular Dynamics (MD) simulations using diblock copolymers as a target system of topical interest.

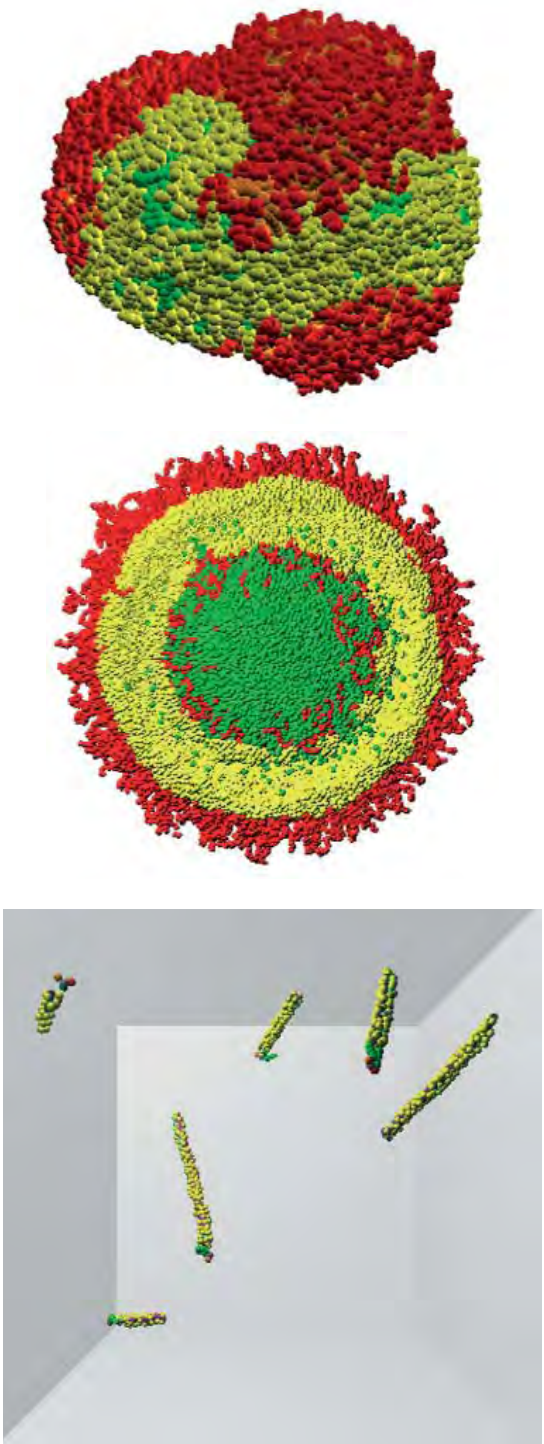

Fig. 1: Illustrations of a two-component vesicle (Illya, PhD Thesis, 2004), a 40 nm polymersome (Ortiz et al., 2005), and growing actin filaments (Shillcock and Lipowsky, in progress). Note that the images are not to the same scale.

Amphiphilic membranes are ubiquitous in nature, and have important technological applications as well. Ms Gregoria Illya, who graduated in December 2004, has used DPD simulations to map out the dependence of amphiphilic membrane structural properties (area per molecule, thickness, density profile) and material properties (lateral stress profile, area stretch modulus and bending modulus) for a homologous series of amphiphiles **[2]**. Mixed membranes containing two types of amphiphile with different tail lengths have also been investigated. For amphiphiles that mix ideally, the membrane area stretch modulus is a non-monotonic function of the composition, in agreement with mean field theories. Amphiphiles that tend to phase separate in the membrane form domains whose shape changes from small circular patches, through stripes, to inverted circular patches as the concentration of the close-packed amphiphile is increased.

Diblock copolymers form closed vesicles called Polymersomes. These systems are of great interest as drug delivery vehicles, amongst other applications, because they are more robust than lipid vesicles, and their material properties can be systematically varied depending on the molecular details of their constituents **[3]**. Together with the group of Prof. Dennis Discher at University of Pennsylvania, we have used DPD simulations to study the properties of polymersomes. We have calibrated the parameters of our DPD diblock model using the Penn group's all-atom and coarse-grained MD simulations. The results are currently being submitted **[4]**, and show that the common assumption in DPD simulations to date that all beads have a common density must be abandoned if the physical properties of the diblock model are to match those of the corresponding experimental system.

The second part of our work is the study of dynamic processes on a mesoscopic scale. As a model system, the fusion of a 28 nm vesicle to a 50 x 50 nm^2 patch has been simulated for up to 2 microseconds using two protocols. The first places the vesicle and membrane patch under initial tensions, and lets the system evolve without further interference. The second protocol places an initially relaxed vesicle next to a relaxed planar membrane patch, and uses a sequence of bending and stretching forces, mimicing the actions of the fusion proteins, to drive the fusion process. The tension-controlled fusion depends sensitively on the size of the membrane patch to which the vesicle fuses and, for the 50 nm patch used here, predicts a pore formation time (measured from the time of first contact between vesicle and planar membrane) of 200-300 ns. This is far below the current experimental resolution of fusion, showing that coarse-grained simulations can already explore regimes that are not yet experimentally characterised. These results have recently been accepted for publication **[5]**. The fusion of membranes with novel molecular architectures and material properties is being extended by a recently-arrived post-doctoral fellow, Dr Lianghui Gao, and a new PhD student, Ms Andrea Grafmüller. The second protocol is still being developed, and we aim to compare the forces required to drive fusion with experimentally-measured forces **[6]**) in order to make predictions about the minimal molecular machinery that can produce reliable vesicle fusion.

Finally, we are using DPD to simulate the self-assembly of actin filaments. Within the framework of a Human Frontier Science Project grant, we are exploring a model of Formin-mediated filament assembly. Formin is a protein that sequentially adds actin monomers to a growing filament while maintaining a constant "grip" on the filament. The monomers bind using non-covalent forces; the filaments are polar, with different growth/shrinkage rates at each end; and the filament stiffness is sensitive to the nature of the bonds holding monomers together. This system has been the subject of recent experimental work **[7]**, and we hope to measure the force exerted by a formin molecule bound to a small bead on a growing filament.

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Properties of Thermally Fluctuating Vesicles

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Properties of Thermally Fluctuating Vesicles

All forms of life are based on the principle of screening small regions from the chemical conditions of the surrounding. Lipid membranes are an excellent material for this purpose. Vesicles basically consist of a closed fluid membrane shell, which is impermeable for most larger molecules. On the other hand, lipid membranes can be penetrated by water molecules and due to their fluidity they can adapt to steric constraints imposed by the environment **[1]**. The research on vesicles provides much insight into the behavior of living cells. Many mechanical and chemical cell properties can be mimicked using lipid membranes and vesicles. An effect that depends on chemical and mechanical properties is the formation of solid domains in a fluid membrane of a vesicle **[2]**. We investigate the stability of different domain shapes by a comparison of their free energies **Fig. 1**.

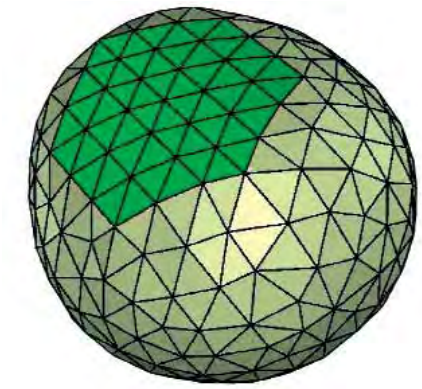

Fig. 1: Model of a vesicle with a solid domain.

Vesicles are not only important to mimic cell properties they can also be used as transport vehicles for the specific application of medically active agents. Not only do they protect their load in the inside from immune reactions of the body, there is also evidence that they can squeeze through small skin pores **[3]**. An investigation of this effect is discussed in the last paragraph.

At first, some more basic aspects are discussed, namely the spontaneous asphericity of free vesicles and a method to measure the binding free energy of vesicles adhering to a substrate.

Basic Properties of Vesicles

The deformation of lipid membranes results in a change of the bending energy. In the simplest case the membrane has no spontaneous curvature, which means, it is preferentially flat. The bending energy is proportional to the bending rigidity κ.

In the presence of larger molecules that cannot permeate through the membrane, an osmotic pressure acts on the vesicle. These molecules are therefore called "osmotically active". The pressure vanishes if the vesicle reaches a volume where the concentration of osmotically active molecules in- and outside the vesicle is equal. In this way, the volume of the vesicle can be controlled by the external molecular concentration.

Free Fluid Vesicles are not Exactly Spherical

We consider a vesicle with no spontaneous curvature in the absence of osmotically active molecules. For very low temperatures, the vesicle assumes the shape with the lowest configurational energy, which is a sphere. For finite temperatures it is often assumed that the vesicle performs small fluctuations around the preferred spherical shape. This is, however, not true. In Monte Carlo simulations we have calculated the free energy F(d) as a function of the order parameter d, which is a measure for the asphericity of the vesicle **[4]**. The parameter d is positive for prolate vesicle shapes, negative for oblate shapes, and zero for sphere-like vesicles. In **Fig. 2** a typical plot of F(d) is shown, which has two minima at about d=+0.1 and d=-0.1, which are the preferred degrees of asphericity. At d=0 there is a distinct maximum, which means that the vesicle is preferentially aspherical. A similar behavior still exists for a small osmotic excess pressure inside the vesicle, which generally stabilizes the sphere shape. For higher excess pressures, the maximum at d=0 vanishes.

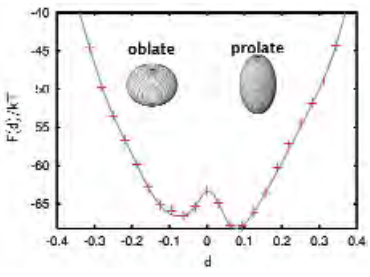

Fig. 2: Free energy F(d) of the asphericity d.

Vesicles Adhering to a Substrate

In living organisms as well as in biomimetic systems, cells or vesicles are often adhering to a substrate. Prominent examples are biosensors in which cells are in contact with metallic electrodes **[5]**. An important quantity is the adhesion strength W, i.e. the adhesion energy per adhering membrane area. It depends on the material properties of the membrane and the substrate and is often difficult to measure in the experiment.

With Monte Carlo simulations we studied systematically the adhesion behavior of a vesicle with a total area A and bending rigidity κ as a function of the temperature T, the adhesion strength W, and the range s of the adhesion potential (see **Fig. 3**).

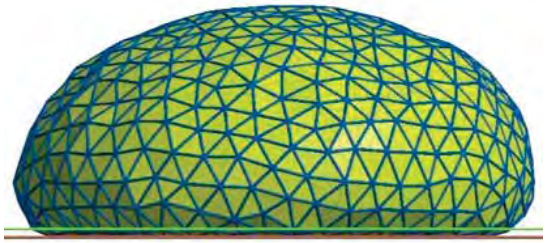

Fig. 3: Snapshot of an adhering vesicle.

We considered vesicles in the absence of osmotically active molecules **[6]** as well as vesicles with osmotically stabilized volumes V. In both cases it is found that the relative adhesion area A_{ad}/A is a linear function of T/κ if the temperature is not too large. An example is given in **Fig. 4**. With and without osmotically active molecules the dependence of A_{ad}/A on the parameters W, κ, T, s, and, eventually, V can be expressed in a simple formula. If s is approximately known and κ is not strongly temperature-dependent, the formulas can be used to determine W and κ by measuring the adhesion area for two different temperatures.

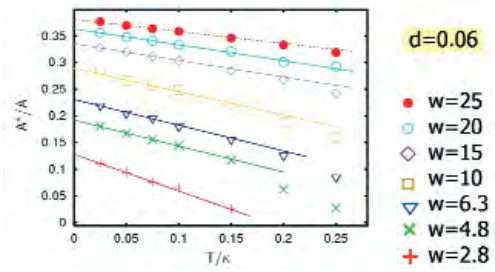

Fig. 4: Relative adhesion area A_{ad}/A as a function of T/k for various values of $w=WA/(2\pi\kappa)$.

Vesicle Transport through Small Pores

A pharmacological application of vesicles is the transport of medically active substances. One important aspect is the transport of vesicles through skin pores which allows carrying active agents into deeper skin regions. It is predicted that the vesicles are pushed through a skin pore by a transdermal concentration gradient of osmotically active molecules. With the help of computer simulations we have found that different molecular concentrations c_1 and c_2 on each side of a small pore is indeed able to drag a vesicle through it **(Fig. 5)**. In the simulations we calculate the free energy barrier $F(A_2)$ for the partial area A_2 having passed the pore. As shown in **Fig. 6** the barrier vanishes for a sufficiently large concentration c_1 and the vesicle is pushed through the pore. The time needed to pass the pore was estimated to be about 70 seconds.

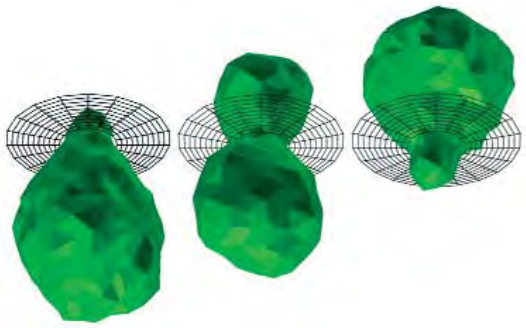

Fig. 5: Snapshots of a vesicle moving though a pore.

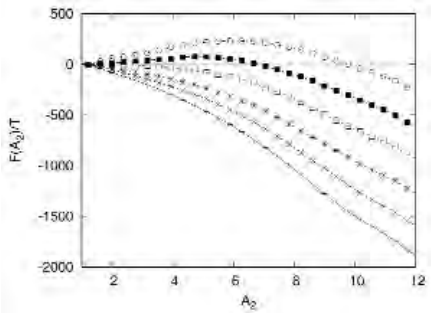

Fig. 6: Free energy barrier for a vesicle moving through a pore.

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Ions Interacting with Membranes and Polymers and in-between Comes Water

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Ion-membrane interactions are important for the physiological activity of cells as they are inherent to almost every cellular process. Synthetic polymers on the other hand are artificial analogs to macromolecules like proteins and nucleic acids whose conformation and properties also strongly depend on the presence of ions. One example of ion-protein interactions is the renowned but still poorly understood Hofmeister series, which arranges different ions according to their ability to induce precipitation of egg white proteins. Overall, the behavior of both, membranes and polymers (artificial or natural), is influenced by interactions with ions. Intuitively, one would expect that electrostatic forces have the most prominent contribution to these interactions. However, the experiments we have performed in the last few years show that the polar character of a trivial molecule like water plays an even more important role. We have found that changes in water structure, i.e., destroying and reforming hydration shells, breaking hydrogen bonds, appears to be the driving force in many ion-membrane and ion-polymer interactions.

A convenient technique for studying these processes is isothermal titration calorimetry (ITC). ITC can be used to measure ion-membrane and ion-polymer interaction enthalpy. When an appropriate model is applied, the titration calorimetry data can be used to extract the equilibrium constant of the process, i.e., characterize the stoichiometry of the interaction. Calcium, chromium and lanthanide ions (like europium and gadolinium) are among the ions that have been studied in our lab **[1-3]**. They were used to probe the properties and stability of large unilamellar vesicles (~100nm in size). All of the ions yield endothermic signals when titrated into the vesicle solution. Even when the lipid membrane is negatively charged, calcium was found to interact with an endothermic signal ($\Delta H>0$) **[1]**.

The results obtained were consistent with measurements investigating ion-polymer interactions. We studied adsorption of calcium to polymers having the same functional groups as those of the charged membranes **[4]**. Once again, the driving factor of the process was found to be the entropy gain from liberating water molecules (see **Fig. 1B**).

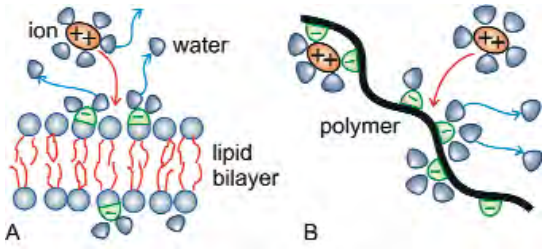

Fig. 1: Schematic presentation of the interaction of a multivalent cation with a negatively charged lipid bilayer (A) and with a polymer (B). The ion size is exaggerated for clarity. The process is driven by the liberation of water molecules from the hydration shells of the ions and the membrane/polymer charges.

The interaction of calcium with polymers was also studied in the context of crystal growth and scale inhibition. In a similar fashion, binding of polymers to calcite crystals was found to be endothermic and entropy driven **[5]**. This indicates that structure of water plays an important, currently not fully recognized role in the control of mineralization processes.

We have found that the ion-membrane and ion-polymer interaction is endothermic ($\Delta H>0$). For the measured processes to occur spontaneously, the condition $T\Delta S>0$ (where T is temperature and ΔS is entropy change) has to apply which implies that the interactions are entropically driven. The gain in entropy is presumably due to destruction and reassembly of hydrations shells finally resulting in the liberation of water molecules, see **Fig. 1**. All of our results point to the importance of the restructuring of water as a driving force in ion-membrane and ion-polymer interactions.

In addition to the thermodynamic characterization we are able to observe the ion-membrane interaction directly using microscopy. Our measurements on giant unilamellar vesicles (~10μm in radius) show that multivalent ions induce adhesion between two neutral membranes **[2, 3]**. In addition, small amount of europium or calcium ions were found to cause membrane rupture presumably due to ion-generated membrane tension. The current working hypothesis is that the ions have condensing effect on lipid molecules, i.e. they reduce the area per lipid, thus bringing about membrane tension and causing eventual rupture.

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Effect of Electric Fields on Model Membranes; "Squaring" the Vesicle

The interaction of electric fields with lipid membranes and cells has been extensively studied in the last decades. The phenomenon of electroporation is of particular interest because of its vast use in cell biology and biotechnology. Strong electric pulses of short duration induce electric breakdown of the lipid bilayer. The membrane becomes permeable for a certain time because of transient pores across the bilayer allowing the influx/efflux of molecules. Thus, electroporation is often used to introduce molecules like proteins, foreign genes (plasmids), antibodies, or drugs into cells. Even though a lot is known about the phenomenology of cell electroporation, the mechanism of pore opening across the lipid matrix is still not fully understood. Experiments on giant vesicles are of special relevance because their size is comparable to cells and allows for direct observation using optical microscopy. In the presence of electric fields, lipid vesicles are deformed because of the electric stress imposed on the lipid bilayer given by the Maxwell stress tensor. This effect has been studied theoretically both for alternating fields and for square-wave pulses **[1]** but few experiments have been performed so far.

The application of AC fields induces shape transformations on giant vesicles. The experiments in our lab (PhD project of Said Aranda) show that phospholipid vesicles subject to AC fields undergo prolate or oblate shape deformation depending on two factors: the frequency of the applied field, ω, and the conductivity ratio between the solution inside and outside the vesicle, σ_{in}/σ_{out}. Based on our results we have constructed a phase diagram that describes the vesicle morphology in response to ω and σ_{in}/σ_{out}.

Microscopy observation of effects caused by electric DC pulses on giant vesicles is difficult because of the short duration of the pulse. Recently this difficulty has been overcome in our lab. Using a digital camera with high temporal resolution we were able to access vesicle dynamics on a sub-millisecond time scale (1 image every 33 µs) **[2]**. The shape deformation induced on lipid vesicles by square-wave pulses was found to depend strongly on σ_{in}/σ_{out}. In the absence of salt spherical vesicles assume a prolate shape as a response to the external field, with the long symmetry axis aligning parallel to field direction, see **Fig. 1**.

For strong enough pulses, electroporation was observed generally accompanied by formation of visible macropores in the micrometer size range **(Fig. 1)**. The response of the system (change in the vesicle aspect ratio, pore lifetime and pore radius) was interpreted in terms of membrane properties like stretching and bending elasticity, surface viscosity, edge energy, and the media viscosity **[2]**.

In addition, the conductivity ratio was demonstrated to play an important role on the vesicle deformation. Depending on σ_{in}/σ_{out} the vesicle can assume prolate or oblate shapes, similar to results obtained in experiments on vesicles in AC fields. Moreover, the DC pulses induce cylindrical deformation as observed for the first time in our lab **[3]**, see **Fig. 2**. Surprising barrel-like shapes were seen only in the case when salt was present in the vesicle exterior.

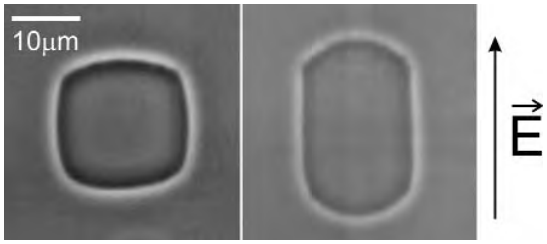

Fig. 2: "Squared" vesicles. In presence of salt in the vesicle exterior high voltage pulses induce short-lived "squared" shapes (due to axial symmetry around the field direction the vesicles should actually be cylindrical).

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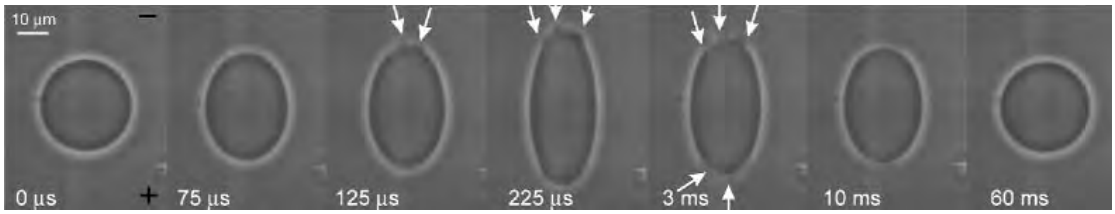

Fig. 1: A snapshot sequence of a vesicle subjected to a pulse of strength 2 kV/cm and duration 200 µs. The vesicle assumes prolate shape elongated along the field direction (the electrode's polarity is indicated with a plus and a minus sign on the first snapshot). Macropores are first visualized in the third frame (125 µs).

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Thermal Fluctuations and Elasticity of Lipid Membranes

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Important model systems for biological membranes are phospholipid bilayers, which are intensively studied with regard to structure, phase transitions, transport and elasticity properties, as well as interaction with other macromolecules. From the point of view of statistical mechanics they represent an interesting class of fluctuating quasi two-dimensional objects whose thermal fluctuations are governed by the intrinsic bending rigidity κ. The effect of the thermal fluctuations on the positional correlations and the scattering intensity distribution has been worked out in the framework of linear elasticity theory (Caillé model) for stacks with periodic boundary conditions, as a function of κ and the compressional modulus B (given by the second derivative of the interaction potential between two membranes at their equilibrium distance d). Recently, the model has been extended to include the boundary condition of a flat substrate on which a stack of lipids can be deposited **[1-4]**.

X-ray experiments to study thermal fluctuations of lipid membranes have been carried out on samples with several hundreds of highly oriented membranes deposited on silicon surfaces and studied at full hydration under excess water **[5]**. The main aim was to map the diffuse scattering over a wide range of momentum transfer, see **Fig. 1** (a), both in radial q_r (parallel to the plane of the membrane) and q_z. Diffuse x-ray reflectivity measurements using 20 keV synchrotron beams have been carried out at the undulator beamline ID1 (ESRF), using both a fast scintillation counter and a multiwire area detector. Data was collected on the uncharged lipids DMPC and POPC. For data acquisition the angles of incidence were chosen so that specular Bragg peaks are not excited. The typical intensity distribution on the CCD detector then consists of only a weak specular beam and two to four strong equidistant diffuse Bragg sheets. From the q_z value, the mean distance d can be obtained, i.e. for fully hydrated DMPC membranes $d \approx 63$ Å, corresponding to a water layer of about 25 Å in between adjacent membranes. Importantly, the width (HWHM) of the diffuse Bragg sheets along q_z increases quadratically with q_r, before it saturates at high q_r, see **Fig. 1** (c) for a typical data set. The quadratic increase (solid line) is in line with the theoretic prediction and its steepness is given by the fundamental smectic length $\lambda = (\kappa / Bd)^{0.5}$. From the analysis of the q_z-integrated intensity the height–height correlation function can be determined using a back transformation method. The resulting curve for DMPC in the fluid phase is shown in **Fig. 1**(c) along with theoretic curves (solid lines) **[4]**. The parameters κ and B can be chosen to fit the curves at small, intermediate or large r, but should be regarded as effective parameters, which can vary significantly since the model cannot account for all data simultaneously.

Already on the level of the raw data, deviations from the predicted behavior are observed: (i) for the power law exponent of the intensity decay shown in **Fig. 1** (d), and (ii) for the saturation of the Bragg sheet width shown in **Fig. 1** (b). Both are observed at parallel wave vector components which were not accessible before (in randomly oriented bilayers or at less brilliant sources). Therefore we must conclude that fluctuations on the corresponding length scales are not well described by the Caillé model. A number of reasons could limit the applicability of the model: (i) non-bending collective motions, (ii) non-linear elasticity terms, (iii) a length scale dependence of *K*, (iv) breakdown of the mean field approach. Alternative more rigorous theories (renormalization group theories, self-consistent theories) and computer simulations on reasonably large stacks of membranes and lateral system size may help to gain more understanding.

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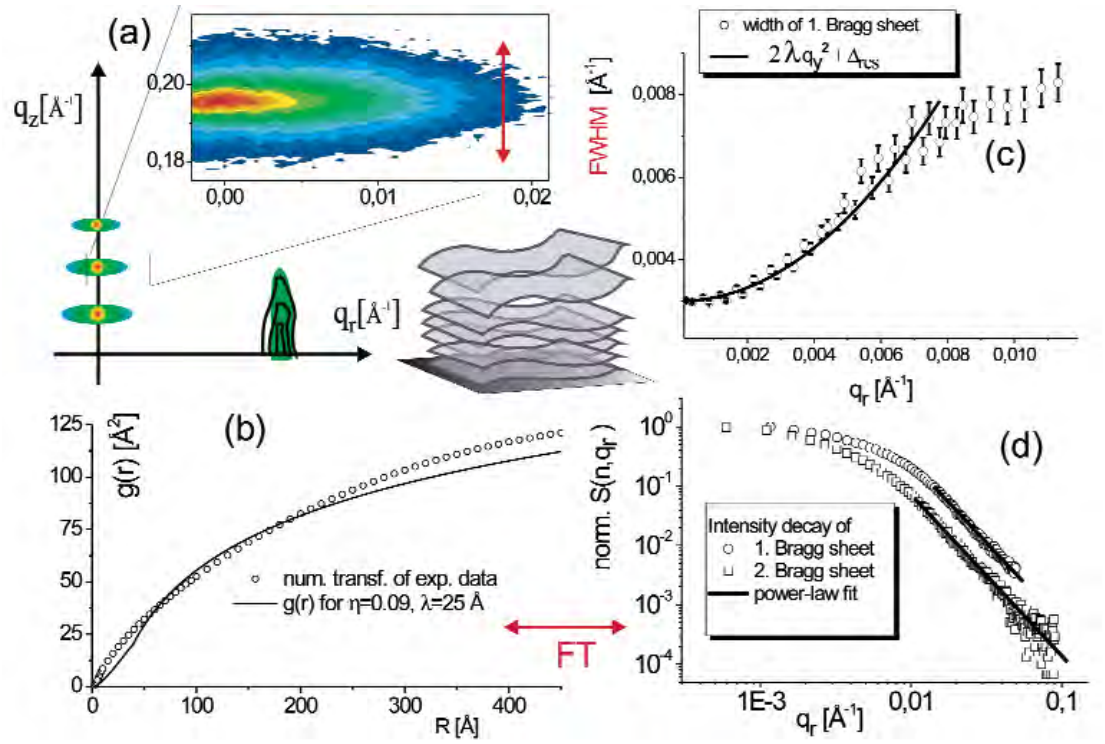

Fig. 1: (a) Typical diffuse scattering distribution of multilamellar lipid bilayers (DMPC, fluid phase) (b) Characteristic height-height self-correlation function of an averaged membrane in the stack as derived from the data, together with theoretic function acc. to [4]. (c) Increase in the width (vertical q_z-width) of the first Bragg sheet. (d) Decay of the (qz-) integrated intensity of the the first two Bragg sheets n=1 and n=2.

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Membrane Adhesion

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In the classic fluid-mosaic model of Singer and Nicolson, biological membranes are envisioned as lipid bilayers with embedded or adsorbed proteins. Recent research on membranes emphasizes two important 'updates' of this picture: First, biological membranes contain *domains* of different composition, and second, *active processes* play a central role for many membrane functions. Our theoretical models of membranes and membrane adhesion are focused on these two novel aspects.

In principle, the formation of membrane domains can be driven by a demixing of the lipid bilayer, or by the aggregation of membrane proteins. Our research here focuses on protein aggregation, in particular during membrane adhesion. The adhesion of biological membranes is mediated by various types of receptors and ligands, also called 'stickers'. These stickers often differ in their characteristic binding lengths. The length difference leads to an indirect, membrane-mediated repulsion between long and short stickers, simply because the lipid membranes have to be curved to compensate the length mismatch, which costs bending energy. The membrane-mediated repulsion causes a lateral phase separation into domains containing short and domains containing long stickers (see **Fig. 1**). In general, the lateral phase behavior depends on the sticker concentrations. Lateral phase separation can only occur if the sticker concentrations exceed a critical threshold. An additional driving force for phase separation comes from large, repulsive glycoproteins, which form a steric barrier for the binding of short stickers. The rich equilibrium phase behavior of such membranes can be characterized using scaling estimates and Monte Carlo simulations.

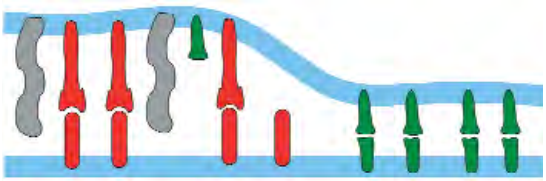

Fig. 1: Domain formation in membranes adhering via short (green) and long (red) receptor-ligand complexes, or 'stickers'. The domains are caused by the length mismatch between the complexes. Repulsive glycoproteins (grey) pose a steric barrier for the short sticker complexes and constitute an additional driving force for the domain formation.

The protein domains in biological membranes are often highly dynamic. Intriguing examples are the domain patterns formed during T cell adhesion. The patterns are composed of domains which either contain short TCR/MHCp receptor-ligand complexes or the longer LFA-1/ICAM-1 complexes. The domain formation is driven by the length difference between the TCR/MHCp and the LFA-1/ICAM-1 complexes. During T cell adhesion, the domains evolve in a characteristic pattern inversion: The final pattern consists of a central TCR/MHCp domain surrounded by a ring-shaped LFA-1/ICAM-1 domain, whereas the characteristic pattern formed at intermediate times is inverted with TCR/MHCp complexes at the periphery of the contact zone and LFA-1/ICAM-1 complexes in the center.

We have studied the pattern formation dynamics in a statistical-mechanical model for the adhesion of multicomponent membranes [**1,3**]. In this model, the adhesion geometry of the cells is taken into account by dividing the membranes into a contact zone and a non-adhering membrane region (see **Fig. 2**).

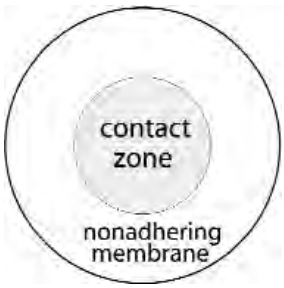

Fig. 2: Cell adhesion geometry. The circular contact zone is surrounded by a nonadhering membrane ring. Receptors, ligands, and glycoproteins diffuse around in the whole membrane, but interact with the apposing membrane only within the contact zone.

We consider the pattern formation in Monte Carlo simulations (see **Fig. 3**) and propose a novel self-assembly mechanism for the formation of the intermediate inverted T-cell pattern. This mechanism is based (i) on the initial nucleation of numerous TCR/MHCp microdomains, and (ii) on the diffusion of free receptors and ligands into the cell contact zone. The diffusion of receptors and ligands into the contact zone leads to the faster growth of peripheral TCR/MHCp microdomains and to a closed ring for sufficiently large TCR/MHCp concentrations. At smaller TCR/MHCp concentrations, we observe a second regime of pattern formation with characteristic multifocal intermediates, which resemble patterns observed during adhesion of immature T cells or thymozytes. The formation of the final T-cell pattern requires active cytoskeletal transport processes in our model, in agreement with experimental findings **[3]**.

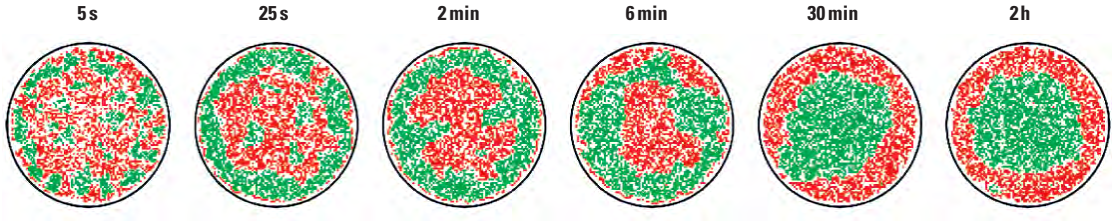

Fig. 3: Simulated pattern formation during T cell adhesion. Within the first minute of adhesion, a peripheral ring of short TCR/MHCp complexes (green) is formed, surrounding a central domain of long ICAM-1/LFA-1 complexes (red). After 30 minutes, this pattern is inverted and a central TCR/MHCp domain emerges.

Active processes also play a role in controlling the adhesiveness of biological membranes. We have considered a simple theoretical model of membranes with active adhesion molecules, or 'stickers' **[4]**. The stickers are actively switched 'on' or 'off', which keeps the system out of thermal equilibrium. We find that the phase behavior of the membranes depends rather sensitively on the switching rates of the stickers and not only on the fraction of 'on'-stickers. In asymptotic regimes of 'slow' and 'fast' switching, we obtain exact results that relate the unbinding behavior of the active membranes to well-studied properties of equilibrium membranes. At intermediate switching rates, we observe resonance and weak binding in Monte Carlo simulations. These results may provide insights into novel mechanisms for the controlled adhesion of biological or biomimetic membranes.

Membranes elastically mediate interactions also between curved objects adhering to them **[2]**. These membrane-mediated interactions are related to those between long and short stickers. The adhesion of curved objects such as rods or beads causes a local perturbation of the equilibrium membrane shape, which leads to the indirect, membrane-mediated interactions. For a planar membrane under a lateral tension, the interaction between two parallel rods is repulsive if the rods adhere to the same side of the membrane, and attractive if the rods adhere at opposite membrane sides. For a membrane in an external potential, the membrane-mediated interactions between adsorbed rods are always attractive and increase if forces perpendicular to the membrane act on the rods.

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Mastering Membrane Fusion

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Membrane fusion is an exciting but relatively complex phenomenon. In real cells it involves the participation of a number of so called fusogenic proteins who are thought to perform the role of a recognition system that brings two membranes together, perturbs the lipid bilayers, and eventually assists the lipid mixing. The fusion process is of significant importance as it is involved in vital cellular functions like import of food stuff and export of waste (endo- and exocytosis), fertilization, signaling in nerve cells and others. Experimental tools for the controlled fusion of membranes should be essential in order to improve and optimize fusion applications like drug delivery, artificial fertilization and gene transfer.

Thus, achieving control on fusion has been the driving force for initiating experiments on model membranes. The most popular bilayer system on which fusion was studied are solutions of small unilamellar vesicles (LUVs) of ~100nm in size. However, in such systems the fusion efficiency is set rather indirectly, the measured properties are determined by the bulk solution (and not by individual vesicle pairs) and thus represent averages over a large number of vesicles. In addition, due to the small size, the behavior of LUVs may be governed by membrane tension and high curvature effects. In contrast, applying optical microscopy to follow interactions between giant unilamellar vesicles (GUVs) gives access to direct observation of fusion events. The GUV size (~10μm) brings the model systems up to the level where the membrane dimensions are of cell-size. In the last decade, several powerful tools such as micropipette aspiration have been developed to allow the experimental manipulation of GUVs. Combining optical microscopy with micropipettes is a rather promising route for studying and achieving control over membrane fusion.

Recently, the investigation of two types of fusion-inducing mechanisms in GUVs was initiated in our lab. In one of them, the inter-membrane interaction is triggered by metal ions forming complexes between functionalized molecules in the bilayers. In the second approach, we apply strong electric pulses to vesicles in contact. In both cases fusion is induced. Using high speed digital imaging we follow the evolution of the fused membranes with unprecedented time resolution of about 50μs. Fusion dynamics as reported in the literature has been limited, so far, to time resolution of about 1ms. For the first time, we were able to observe the opening of the fusion pore with high temporal resolution.

Fusion of Functionalized Membranes:
The membranes are functionalized with synthetic fusogenic molecules **[1]** which can form a complex with multivalent ions. The fusogenic molecules have a lipid-like structure with hydrophilic headgroup containing a specific ligand. The ligands form coordination complexes with metal ions in 2:1 ratio. When the complexes are formed between ligands from opposing membranes, the expected event is fusion. This fusion scenario was probed in our lab **[2]** by means of manipulating two vesicles with micropipettes. A third micropipette was used to locally inject a solution of multivalent ions. The ions were observed to induce adhesion between the two vesicles, which was followed by fusion. **Fig. 1** is a simplified cartoon of the possible fusion mechanism occurring at molecular level. The resolution of optical microscopy (~0.5μm) limits the observation to the micrometer scale and the molecular events cannot be revealed. Thus it is not clear how many complexes are involved in the fusion event.

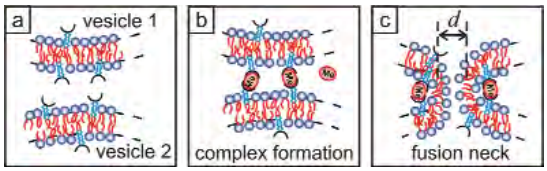

Fig. 1: Possible steps in the fusion of functionalized membranes: (a) two functionalized lipid vesicles are brought into contact; (b) a solution of multivalent ions is locally injected in the contact area leading to the formation of inter-membrane complexes; (c) the opening of the fusion neck is initiated.

Electrofusion:
When exposed to weak AC field, vesicles align in the direction of the field. This can bring two vesicles into contact. The subsequent application of DC pulses leads to charging of the membrane. This creates transmembrane potentials which are enhanced at the vesicle poles (facing the electrodes). The corresponding compression of the membrane effectively induces tension. DC pulses can lead to perforation of the membrane in two cases **[3]**: (i) when the transmembrane potential exceeds some critical value (~1V); or (ii) when the total membrane tension approaches the lysis tension of the membrane (~5dyn/cm). When poration is induced in the contact area of two vesicles, fusion is expected to occur. **Fig. 2** illustrates a possible mechanism of electrofusion of two bilayers in contact.

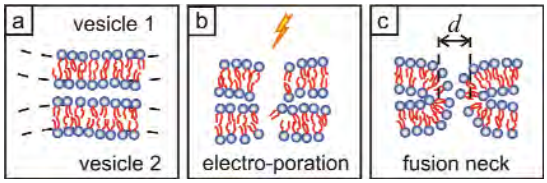

Fig. 2: Possible steps in electrofusion: (a) two lipid vesicles are brought into contact and aligned using AC field; (b) a short electric pulse is applied causing membrane poration; (c) the lipids from the opposing bilayers mix initiating the opening of the fusion neck.

In the experiments, the vesicles are placed between two electrodes and then observed with phase contrast microscopy. One example of a fusion event observed with a fast digital camera and phase contrast microscopy is presented in **Fig. 3**. The two vesicles were aligned by an AC field applied prior to the DC pulse. Time t=0 corresponds to the beginning of the pulse. A closer look at the micrograph sequence (not all of the acquired snapshots are displayed) shows that fusion has already occurred within the first 50µs. Using intensity profile image analysis, we are able to follow the evolution of the opening of the fusion neck diameter, *d*, (see F**ig. 1c** and **Fig. 2c**). The experiments extend over five orders of magnitude in time, ranging from microseconds to seconds. Two characteristic times are revealed, presumably corresponding to two different processes: molecular rearrangement of the lipid bilayers related with relaxation of the edge curvature of the fusion pore (t~1ms), and hydrodynamics of mixing of the fluid contents of the fusing vesicles.

In certain cases, when electrofusion is induced, multiple fusion events are observed (the example in **Fig. 3** illustrates one of them). The reason for this behavior is that the fusing vesicles have porated at several places. This leads to reclosure of the membrane inside the product vesicle and to formation of smaller internalized vesicles (one can see this in **Fig. 3** at t=10s where the internal vesicles appear as brighter spots inside the resulting vesicle; the brighter gray values are due to refractive index mismatch of the vesicle contents).

In conclusion, we have achieved controlled fusion induced by two approaches: ligand mediated fusion and electrofusion. The tools available in our lab have allowed us to reach unprecedented time resolution of the fusion process.

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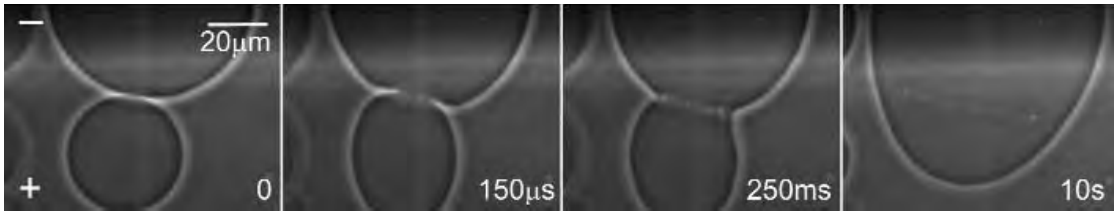

Fig. 3: Snapshot sequences of electrofusion of a vesicle couple. The time is indicated on each snapshot. The electrodes polarity is indicated with a plus (+) and a minus (-) sign on the first snapshots. The image acquisition rate was 30,000fps. The applied pulse has a strength of 90V and a duration of 150µs.

Free and Tethered Polyelectrolytes

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Polyelectrolytes (PELs) are macromolecules that contain subunits having the ability to dissociate charges in polar solvents such as, e.g., water. Due to their importance in materials science, soft matter research, and molecular biology, PELs have received a lot of attention in recent years.

With respect to different dissociation behaviors, one can distinguish between strong and weak PELs, a classification used among chemists, or between quenched and annealed PELs, the common classification in the physics community. Strong PELs, poly-salts such as, e.g., Na-PSS, dissociate completely in the total pH range accessible to experiment. The total charge as well as its particular distribution along the chain is solely imposed by polymer synthesis. On the other hand, weak PELs represented by poly-acids and poly-bases dissociate in a limited pH range only. The total charge of the chain is not fixed but can be tuned by changing the solution pH. The number of charges as well as their distribution is a fluctuating thermodynamic variable. The control parameter is the solution pH which is, up to trivial additive constants, the chemical potential of the charges μ.

Polymer brushes consist of chains densely end-grafted to a surface. Due to various forces, tethered chains are enforced to take an elongated conformation. PEL brushes form the subject of increasing interest in theory, simulation and experiment. From the application point of view, they are an effective means for, e.g., preventing colloids from flocculation. PEL brushes can be used in small devices for pH-controlled gating and are thought to be a model for the protecting envelope of cells (glycocalix).

Annealed Polyelectrolytes in Poor Solvents

We study annealed PELs by semi-grand canonical Monte Carlo simulations where the chains are in contact with a reservoir of charges of fixed chemical potential μ. For sufficiently poor solvent quality, it was recently confirmed **[1]** that the chains undergo a first-order phase transition between a weakly charged globule and a strongly charged stretched conformation as predicted by theory. However in the close-to-Θ-point regime $\tau < \tau^*$ ($\tau = (\Theta - T)/\Theta$) the conformational transition becomes almost continuous. Changing the degree of ionization by tuning the chemical potential, i.e., by tuning the solution pH, we obtain for the first time a sequence of pearl-necklace transitions in annealed PELs (see **Fig. 1 [2]**). Most of the pearl-necklace parameters are found to obey the scaling relations predicted for quenched PELs. Although there occurs a sequence of discrete transitions embedded in the continuous crossover from globule to stretched chain, due to strong fluctuations the pearl-necklace transition as a whole appears to be continuous.

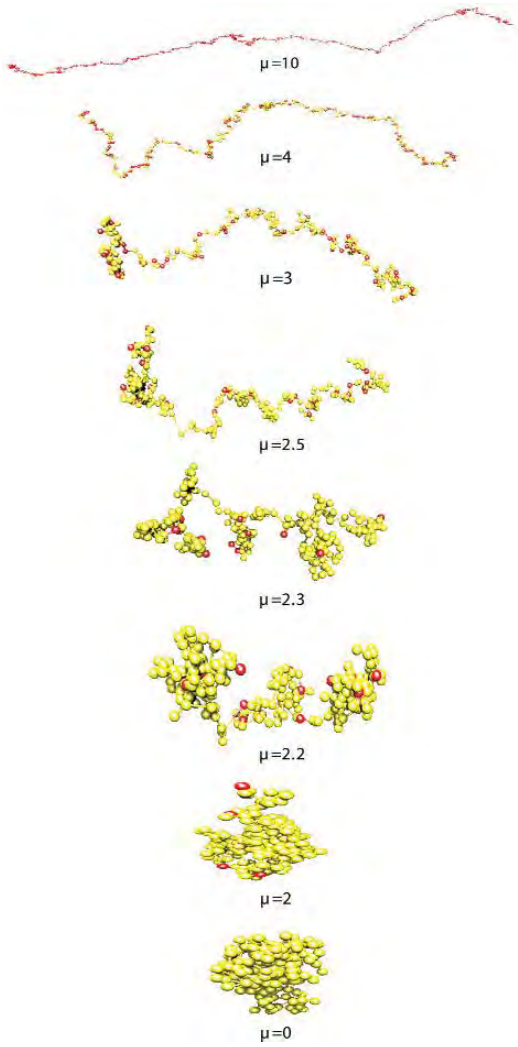

Fig. 1: Annealed PELs, close-to-Θ-point behavior at $\tau = 0.07$ ($\lambda_B/b = 1$, $\lambda_D/b = 10$). Simulation snapshots taken at varying chemical potential μ: globular structure ($0 \le \mu \le 2$), pearl necklaces ($2.2 \le \mu \le 2.5$), stretched chain ($3 \le \mu \le 10$). Charged monomers are colored red, uncharged yellow.

Varying salt concentration is an important parameter to tune the polyelectrolyte effect and to change the structure of PELs in experiment. Due to the additional charge degree of freedom, annealed PELs exhibit a rather complex behavior. **Fig. 2** shows the end-to-end distance R as a function of the screening length λ_D at moderate chemical potential **[3]**. At $\lambda_D/b \lesssim 2$ we recover the behavior known from quenched PELs: starting from a globule the chain becomes increasingly stretched with growing λ_D. An interesting feature is visible at $\lambda_D/b \approx 0.1$ where completely charged pearl necklaces exist. Beyond $\lambda_D/b \approx 2$, however, the chain shrinks again. Due to reduced screening the electrostatic penalty of ionization becomes too large and the chain starts to minimize its energy by a partial neutralization of charge. Thus, the polyelectrolyte effect is suppressed although screening is reduced. Clearly the position of maximum stretching depends on the particular chemical potential.

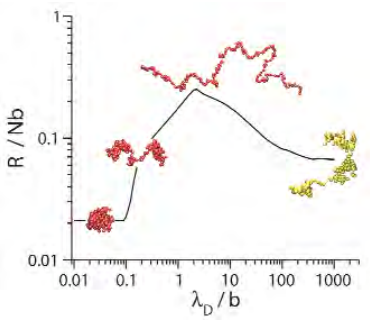

Fig. 2: Annealed PELs, close-to-Θ-point behavior at $\tau = 0.07$ ($\lambda_B/b = 1$, $\mu = 3.0$). Chain extension R vs. screening length λ_D, typical snapshots of the different regimes are shown using the same coloring as in Fig.1.

Polyelectrolyte Brushes

Recently a slight but detectable variation of brush height *h* on grafting density ρ_a has been obtained both in experimental and simulation studies **[4]**. This disagrees with the well-accepted scaling relation in the so-called osmotic brush regime, but can be understood on a semi-quantitative level by using a free-volume approximation: The volume available for the counterions $V_0'' = h / \rho_a$ is reduced by the self-volume of the chain $\upsilon = Nb\sigma_{eff}^2$, where σ_{eff} takes into account the monomer and counterion diameters. Thus the free-volume is given by $V'' = V_0''$ (1 - η), with η being the degree of close-packing in the brush. Balancing the resulting nonlinear entropy of counterions with the high-stretching chain elasticity, the equilibrium brush height depends on ρ_a indeed. **Fig. 3** shows simulation results with various theoretical predictions where the nonlinear theory was evaluated with $\sigma_{eff}^2 = 2\sigma^2$ and σ is the Lennard-Jones radius that governs the range of short-range interaction **[4]**.

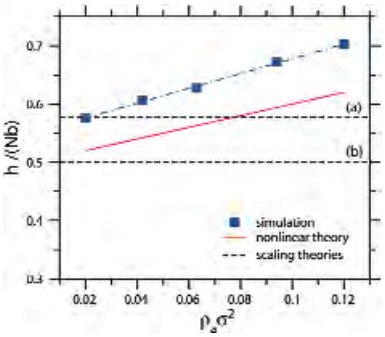

Fig. 3: Brush height as a function of grafting density ρ_a for completely charged polyelectrolyte chains ($\lambda_B/b = 1$). Symbols show simulation data with corresponding linear fit (dot-dashed line); the straight solid line gives the prediction of the nonlinear theory. The dashed lines show previous scaling predictions.

According to Pincus **[5]** the brush shrinks with increasing salt concentration, but only as a relatively weak power law $c_s^{-1/3}$. There is some experimental and theoretical work that confirms this prediction, but there are other results that are in contradiction. With the new simulation code, we are able to consider systems up to about 7200 charges. This allows studying the effect of additional salt ions. **Fig. 4** shows the brush height as a function of the (free) ion concentration inside the brush for two different grafting densities. Note that this ion concentration is caused by salt co- and counterions and original counterions. Finite size effects have been carefully checked. Finally, we observe an almost perfect agreement with the scaling prediction **[6]**.

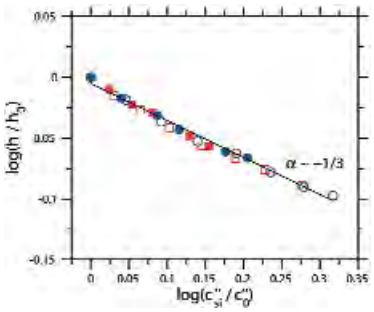

Fig . 4: Brush height as a function the ion concentration inside the brush ($\lambda_B/b = 1$) at grafting density $\rho_a\sigma^2 = 0.04$ (circles) and 0.09 (squares). Simulation results obtained for two different heights of the simulation box: $L_z = 3Nb$ (filled symbols), $L_z = 2Nb$ (open symbols).

Due to the polymer layer close to the anchoring surface, a priori there is a non-homogeneous particle distribution perpendicular to the interface. The first attempt to understand the relation between the concentrations of small ions in the brush and outside the polymer layer at varying salt concentration is by a Donnan equilibrium approach. **Fig. 5** (dashed lines) shows that this fails because of the high concentration in the brush state. However, taking into account the self-volume of PEL chains as indicated above and using the same σ_{eff} we observe a nice agreement with the simulation results for both anchoring densities **[6]**.

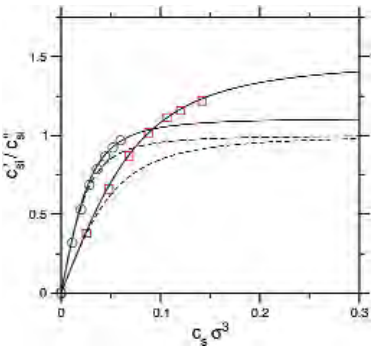

Fig. 5: Relation between the ion concentration inside the brush c''_{si} and buffer concentration c'_{si} for different salt concentration c_s. Simulation results (symbols as in Fig. 4) and predictions of original (dashed) and modified Donnan approach (solid lines).

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Structure Formation in Systems of Mesoscopic Rods

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Mesoscopic structures are a timely research area since new experimental techniques like atomic force microscopy or optical tweezers allow a detailed investigation and manipulation on this length scale. The controlled production of nanostructures on larger scales facilitates the design of new materials, whose mechanical, optical, and chemical properties can be tailored in completely new ways. Inspirations are given from the rich complexity found in molecular cell biology. The controlled production of mesoscopic devices has a wide range of applications reaching from microsurgery, over nanochemistry to a further minimization of microprocessors.

One building block for the creation of nanostructures are mesoscopic rods, which nowadays can be produced in large amounts **[1, 2]**. With the help of Monte Carlo simulations we investigate how structure formation in systems of mesoscopic rods is influenced by the properties of the molecules and the influence of the environment. The results help to control rod systems in such a way that rodlike macromolecules can be used to build ordered superstructures.

Systems of Chemically Homogenous Rods

Mesoscopic rodlike molecules and molecular assemblies **[3]** are typically the product of a linear growth process. Therefore, these rods have the same diameter along their axes. For a fluid phase the rods have to be in a solvent. The steric interaction of the rods can be well described by hard spherocylindric rods (*hr*).

Further, attractive interactions may arise from van der Waals and depletion forces. A simplified model for the complete interaction is found by integrating a square well potential along both rod axes. The resulting attractive rod (*ar*) potential can only be calculated with a large numerical effort.

Instead we have developed an angular-dependent site-site potential (see **Fig. 1**) that mimics the ar potential very well with a computational effort comparable to the *hr* potential.

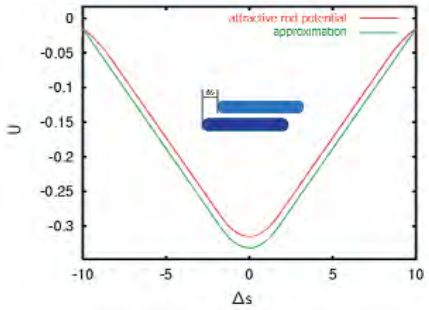

Fig. 1: Attractive rod potential compared with simplified potential.

Caused by the production processes, systems of mesoscopic rods typically have a broad length distribution, while for many applications a narrow length distribution would be favorable. A fractionation of rod lengths occurs in the phase coexistence region of the isotropic and a nematic or smectic phase of the system. For the ar potential the formation of an ordered phase occurs at much lower pressures as for the *hr* potential. In an ongoing project, we compare the nucleation behavior of attractive rods with that for hard rods **[4]**.

A binary 1:1 mixture of rods with lengths L_1=3 and L_2=6 has been investigated in a Gibbs ensemble simulation, in which two simulation boxes are run in parallel **[5]**. The two boxes can exchange rods and volume such that they have the same pressure and chemical potential. In the phase coexistence region the two sorts of particles demix almost completely. **Fig. 2** shows the two boxes before and after the demixing. The plot in **Fig. 3** illustrates the growing number of small rods and the decreasing number of large rods in box (a). In subsequent simulations the behavior of polydisperse mixtures and the influence of adjacent substrates will be investigated.

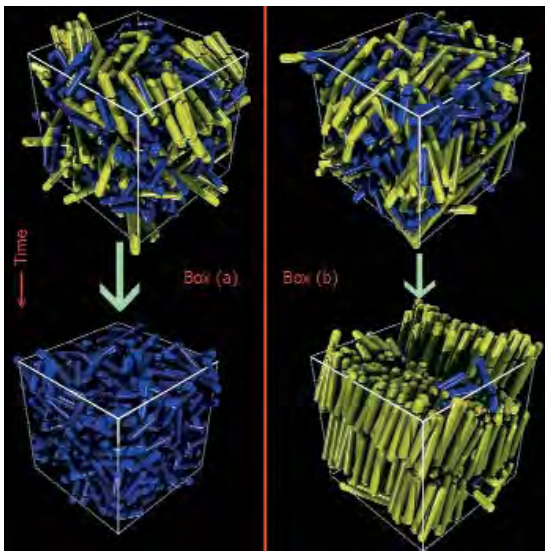

Fig. 2: Demixing of short rods (blue) and long rods (yellow) in a Gibbs ensemble simulation.

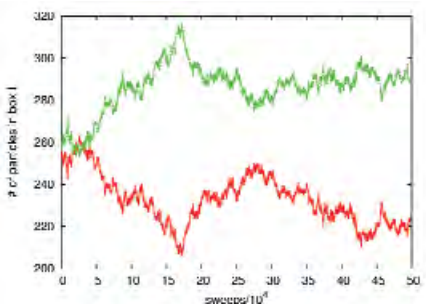

Fig. 3: Time development of long rods (red) and short rods (green) in box (a).

Systems of Chemically Heterogeneous Rods

Mesoscopically large rods can be tailored to have a chemically heterogeneous structure, which provides new types of ordered structures in the rod system. We investigate hard rods with attractive potentials at the end. In large regions of the phase diagram the behavior of such systems is qualitatively similar to that of systems with chemically homogenous rods. At rather low pressure, however, the formation of a three dimensional, scaffold-like network structure is found showing cluster points where the rods meet with a finite angle (see **Fig. 4**). These structures are stabilized by the addition of an angular dependence of the attractive potential. In a next step we will check if a regular scaffold structure, such as the one shown in **Fig. 5** can be thermodynamically stable with an appropriate potential at the rods' ends.

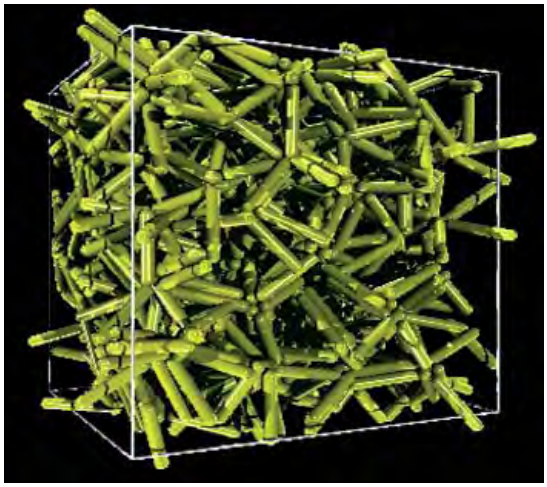

Fig. 4: Ultraporous structure formed by chemically heterogenous rods with attractive endgroups.

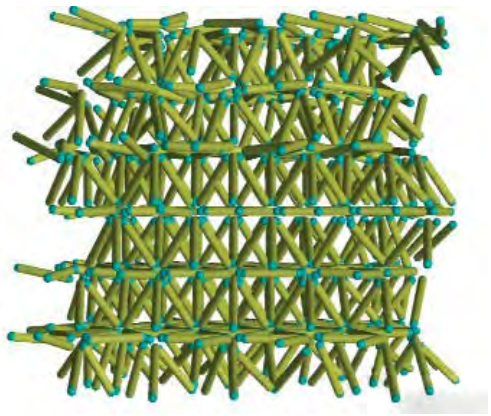

Fig. 5: A scaffold-like fcc-structure is expected to be stable for suitable chemically heterogenous rods.

In another project a system of small rods with attractive ends and long chemically homogenous rods is investigated. This provides a simple model for the cytoskeleton, where the long rods are filaments and the small heterogeneous rods mimic the crosslinkers. Here it will be investigated, how the structure of the filament network depends on the concentration of the crosslinkers.

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The Elasticity of Silk

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The capture silk of orb weaving spiders is much softer than its dragline silk or the silk for web frame and radii. Nevertheless, its tensile strength per unit weight is still comparable to steel; and unlike steel, the spider capture silk is extremely extensible, being stretchable to almost ten times its relaxed contour length without breaking. This perfect combination of strength and extensibility conveys a high degree of toughness to the capture silk: its rupture energy per unit weight is more than 20 times that of a high-tensile steel.

With the aim to produce synthetic silks with similar mechanical properties, materials scientists have devoted many experimental and computational efforts to the understanding of spider silk's structural organization. Nevertheless, the mechanism behind spider silk's remarkable strength and elasticity is still poorly understood, partly because of the difficulty to obtain high-quality crystallized structures of silk proteins.

Single-molecule force spectroscopy methods were recently applied to spider silks to obtain very detailed information on their force-extension response. Hansma and coworkers attached capture silk mesostructures (probably composed of a single protein molecule) or intact capture silk fibers to an atomic force microscopy tip and recorded the response of the samples to an external stretching force. They found a remarkable exponential relationship between the extension x and the external force f,

$$f \propto \exp(x/\ell),$$

where ℓ is the length constant; $\ell = 110 \pm 30$ nm for a capture silk molecule and $\ell = 11 \pm 3$ mm for an intact capture silk fiber. This exponential behavior was observed both in solution and in air within a force range from about 10^0 piconewton (pN) to about 10^6 pN.

The exponential force-extension behavior of spider capture silk is significantly different from the force-extension responses of simple biopolymers such as DNA or titin proteins. The elasticity of a simple biopolymer can usually be well predicted by the freely-jointed-chain model or the semiflexible wormlike-chain model. The exponential force extension response of spider capture silk indicates that it is not a 'simple' biopolymer. The question is: Can one infer the structural organization of the spider capture silk from its force-extension response curve?

The exponential force extension response behaviour indicates the following: (1) Because capture silk is highly extensible, a great amount of extra length must have been stored in its relaxed form.

(2) Since extension increases with force logarithmically, some fraction of the stored length can be easily pulled out, a second fraction is more difficult to be pulled out, and a third fraction is even more so etc.

To model this kind of heuristic response cascade, we proposed a *hierarchical chain model* for spider capture silk. In this model, the polymer is composed of many basic structural motifs; these motifs are then organized into a hierarchy, forming structural modules on longer and longer length scales.

At the deepest hierarchy level h_m, the structural motifs could be β-sheets, β-spirals, helices or microcrystal structures. The interactions among some of these motifs are much stronger than their interactions with other motifs, therefore they form a structural module at the hierarchy level (h_m-1).

These level-(h_m-1) modules are then merged into level-(h_m-2) modules through their mutual interactions. This merging process is continued; and finally at the global scale, the whole spider silk string is regarded as a single module of the hierarchy level h=0. We found that the response behavior of such a model polymer is characterized by an exponential force-extension curve.

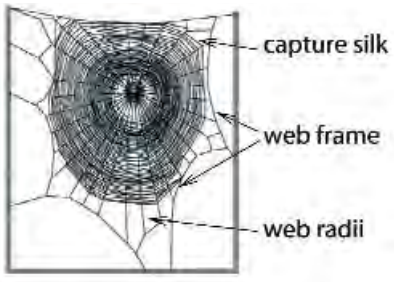

Fig. 1: The web of ***Araneus diadematus****.*

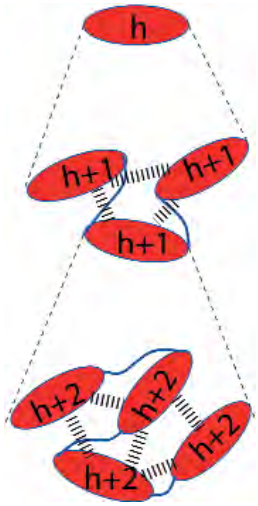

Fig. 2: The hierarchical chain model. At each hierarchy level h a structural module M_h is composed of a tandem sequence of m_h submodules M_{h+1} of hierarchy level h+1. Under external stretching, M_h responds by (i) adjusting the arrangements of its m_h subunits and making them more aligned along the force direction, and (ii) extending these m_h subunits. The thick broken lines between submodules of each hierarchy level indicate the existence of sacrificial bonds, such as weak hydrogen bonds or van der Waals attractions.

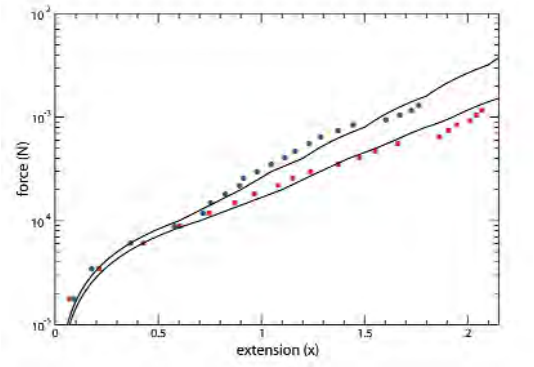

Fig. 3: Exponential force-extension relationship for the hierarchical chain model. Symbols are experimental data from the Hansma group.

Hierarchical chains respond to external perturbations in a hierarchical manner. If the external force is small, only those structural units of length scale comparable to the whole polymer length will be displaced and rearranged; structural units at short and moderate length scales will remain unaffected. As the strength of the external perturbation is increased, additional structural units at shorter length scales are also deformed. Through such a hierarchical organization, a single polymer chain can respond to a great variety of external conditions; at the same time, it is able to keep its structural integrity even under strong perturbations. This hierarchical modular structure also indicates a broad spectrum of relaxation times. The modules at the shorter length scales will have much shorter relaxation times and will be refolded first when the external force decreases. This gap in relaxation times ensures that, after extension, the spider capture silk will return to its relaxed state gradually and slowly. This is a desirable feature for spider capture silk, because a too rapid contraction in response to the insect's impact would propel the victim away from the web.

The simple hierarchical chain model, while appealing, needs further experimental validation. This model seems to be supported by recent genetic sequencing efforts.

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Semiflexible Polymers and Filaments

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Many biopolymers such as DNA, filamentous (F-) actin or microtubules belong to the class of semi-flexible polymers. The biological function of these polymers requires considerable mechanical rigidity. For example, actin filaments are the main structural element of the cytoskeleton which gives the cell unique mechanical properties as it forms a network rigid enough to maintain the shape of the cell and to transmit forces, yet flexible enough to allow for cell motion and internal reorganization in response to external mechanical stimuli. Another important class of semi-flexible polymers are polyelectrolytes where the electrostatic repulsion of the charges along the backbone can give rise to considerable bending rigidity depending on the salinity of the surrounding solution.

The physics of semi-flexible polymers becomes fundamentally different from the physics of flexible synthetic polymers when their bending energy dominates over conformational entropy. The bending stiffness is characterized by the persistence length. On scales smaller than the persistence length, bending energy dominates and qualitatively new semi-flexible behaviour appears. Biopolymer persistence lengths range from 50nm for DNA to the 10μm-range for F-actin or even up to the mm-range for microtubules and are thus comparable to typical contour lengths such that semi-flexible behaviour plays an important role.

Binding and Adsorption

Binding of two polymers and adsorption of a polymer onto a surface **(Fig. 1)** are two phase transitions of fundamental importance. For both transitions, semi-flexibility is relevant and leads to new critical exponents, or changes even the order of the transition **[1,2]**. In contrast to flexible polymers, binding and adsorption transitions of semiflexible polymers are typically *discontinuous*. Semiflexible polymers bind or adsorb more easily the more rigid they are.

Fig.1: Left: Binding of two polymers, Right: Adsorption onto an adhesive surface.

Single Polymer Manipulation

During the last decade micromanipulation techniques such as optical tweezers and atomic force microscopy (AFM) have become available which allow a controlled manipulation of single polymers and filaments. Experiments such as stretching of single DNA polymers or pushing adsorbed polymers over a surface with an AFM tip open up the possibility of characterizing mechanical filament properties on the single molecule level. In order to interpret experiments quantitatively, theoretical models are necessary which allow to calculate the response of a polymer to external forces. We investigated such models for (i) the stretching of semiflexible harmonic chains **[3]**, (ii) the activated dynamics of semiflexible polymers on structured substrates **[4,5]**, and (iii) force-induced desorption.

(i) In order to improve the quantitative interpretation of force-extension curves from stretching experiments on single semiflexible polymers such as DNA or F-actin, we introduced a semiflexible harmonic chain model **[3]**. This model includes not only the bending rigidity, but also takes into account the polymer extensibility, the monomer size and the finite contour length. Our results for this model allow to extract all of these parameters from experimental force-extension curves. (ii) Strongly adsorbed polymers are often subject to surface potentials that reflect the symmetry of the underlying substrate and tend to align in certain preferred directions. If such polymers are pushed over the substrate by a homogeneous force arising, e.g., from hydrodynamic flow or by a point force as can be exerted by AFM tips, their dynamics is thermally activated and governed by the crossing of the surface potential barriers. Barrier crossing proceeds by nucleation and subsequent motion of kink-antikink pairs **(Fig. 2)**. The analysis of this process shows that static and dynamic kink properties are governed by the bending rigidity of the polymer and the potential barrier height **[4,5]**, which implies that experimental measurements of the kink properties can be used to characterize material properties of both the semiflexible polymer and the substrate.

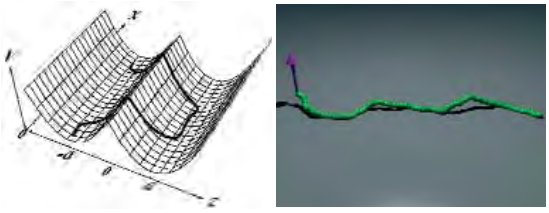

Fig. 2: Left: Kinked conformation of a semi-flexible polymer in a double-well potential. Right: Snapshot of a Monte-Carlo simulation of an adsorbed polymer. A force applied to one polymer end (arrow) can lead to force-induced desorption

(iii) AFM tips can also be used to lift an adsorbed polymer from a surface **(Fig. 2)**. We can calculate the resulting force-extension characteristics for such a force-induced desorption process. One interesting feature is the occurrence of an energetic barrier against force-induced desorption which is solely due to the effects from bending rigidity.

Filament Bundles

Filament assemblies play an important role as functional and structural elements of the cytoskeleton. Using analytical and numerical methods we studied the formation of filament bundles. In the cell, filament bundles are held together by adhesive crosslinking proteins. In a solution of crosslinkers and filaments, the crosslinkers induce an effective attraction between filaments. Starting from analytical results for two filaments **[1,2]**, we have studied this problem analytically for N filaments and numerically for up to 20 filaments using Monte-Carlo simulations **[6]**. Above a threshold concentration of crosslinkers a bundle forms in a discontinuous bundling phase transition **[6]**. This mechanism can be used by the cell to regulate bundle formation. Deep in the bundled phase at high crosslinker concentration, we observe a segregation of bundles into smaller sub-bundles, which are kinetically arrested **(Fig. 3)**. The system appears to be trapped in a glass-like state. Starting from a compact initial state, on the other hand, the bundle reaches its equilibrium configuration with a hexagonal arrangement of filaments **(Fig. 3)**.

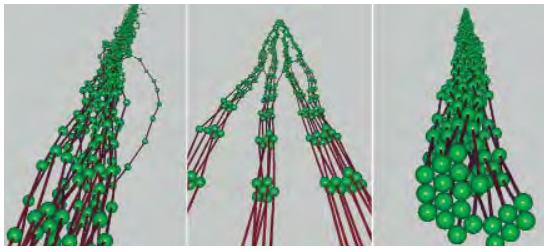

Fig. 3: Monte-Carlo snapshots of filament bundles.
Left: Close to the bundling transition.
Middle: Deep in the bound phase bundles tend to segregate.
Right: Equilibrium shape of the bundle.

Active Filaments

The living cell is an active system where cytoskeletal filaments are not in equilibrium. ATP- or GTP-hydrolysis allows them to constantly polymerise and de-polymerise (treadmilling). The active polymerisation dynamics can be used for force generation. Extending our work on filament bundles, we study force generation by growing filament bundles.

Cytoskeletal filaments not only generate force by active polymerisation but also interact with molecular motors, which are motor proteins walking on filaments by converting chemical energy from ATP-hydrolysis into mechanical energy. The interplay between filaments and molecular motors can give rise to structure formation far from equilibrium. This can be studied in model systems such as motility assays where filaments are adsorbed and actively transported over a glass plate, which is covered with anchored molecular motors. Computer models of such assays allow to predict and quantify formation of filament patterns, e.g., clustering and ordering **(Fig. 4)**. Apart from motor and filament densities, also microscopic motor parameters such as their stall and detachment force determine the emerging pattern and can thus be inferred from the experimentally observed filament structures.

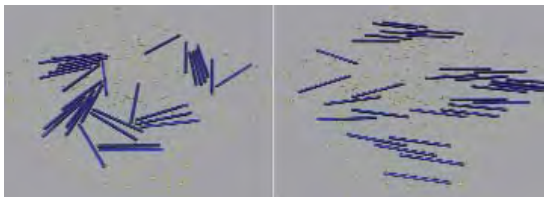

Fig. 4: Snapshot of a motility assay simulation. Filaments (blue) are driven by molecular motors (yellow) over a substrate (grey).
Left: Formation of immobile clusters of filaments blocking each other.
Right: Nematic ordering due to collisions of moving filaments.

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Traffic of Molecular Motors

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Molecular motors are proteins which catalyze a chemical reaction and use the free energy released from this reaction to generate directed movements and to perform work. Examples are the cytoskeletal motors which move in a directed fashion along cytoskeletal filaments, e.g. kinesins which move along microtubules. They consume adenosinetriphosphate (ATP) which represents their chemical 'fuel' and move in discrete steps in such a way that one molecule of ATP is used per step. Our understanding of molecular motors is based on biomimetic model systems which are rather simple compared to biological cells and consist of only a small number of components such as motors, filaments, and ATP. These systems allow us to study the transport properties of molecular motors systematically. A typical biomimetic experiment is shown in **Fig. 1**.

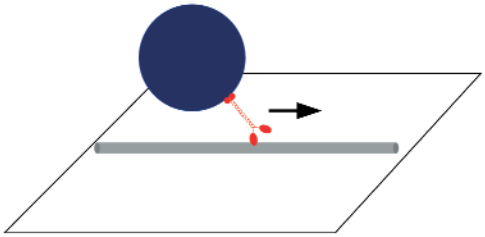

Fig. 1: The bead assay provides an example for a biomimetic model experiment: A molecular motor transports a (glass or latex) bead along a filament which is immobilized on a surface.

Unbinding and Motor Walks

A molecular motor is called processive if it makes many steps while it is bound to the filament. However, even processive motors have only a finite walking distance, because the motor-filament binding energy can be overcome by thermal fluctuations. This walking distance is typically of the order of 1 µm for cytoskeletal motors. Unbound motors perform Brownian motion in the surrounding aqueous solution until they collide again with a filament and rebind to it.

Therefore, on large length and time scales which exceed a few microns and a few seconds, respectively, molecular motors perform peculiar motor walks as shown in **Fig. 2**. These motor walks consist of alternating sequences of active directed movements along filaments and passive non-directed diffusion **[1]**.

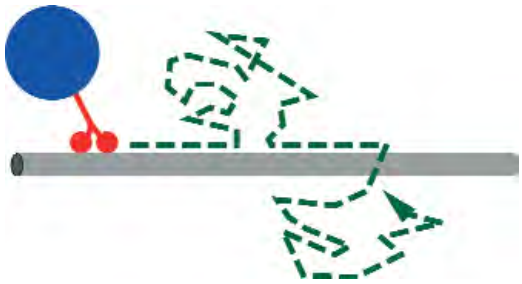

Fig. 2: Motor walks: A molecular motor performs active directed movement along a filament and unbinds from it after a certain walking distance. The unbound motor diffuses passively in the surrounding fluid until it rebinds to the filament and resumes directed motion.

We have studied these motor walks for various compartments with different geometries using both computer simulations and analytical techniques **[1, 2]**. The motor walks exhibit anomalous drift behaviour and strongly enhanced effective diffusion due to the repeated binding to the filament. The enhanced diffusion is particularly pronounced if the walking distance is large, which is the case for motor particles driven by several motor molecules.

Exclusion and Jamming

If the concentration of molecular motors in a compartment is large, motor-motor interactions become important and lead to a variety of cooperative phenomena. In particular, motors interact via simple exclusion or hard core repulsion which implies that a motor bound to a binding site of the filament excludes other motors from this filament site. This type of motor-motor interaction leads to traffic jams on the filament and implies the existence of various kinds of phase transitions. In contrast to the traffic of cars and other vehicles, unbinding from the filament and diffusion of unbound motors play a role in the traffic of molecular motors. We have focussed on tube-like compartments as shown in **Fig. 3** with different kinds of boundary conditions. The tube geometry mimics the geometry of an axon, which provides the most prominent example for long-range motor traffic in vivo.

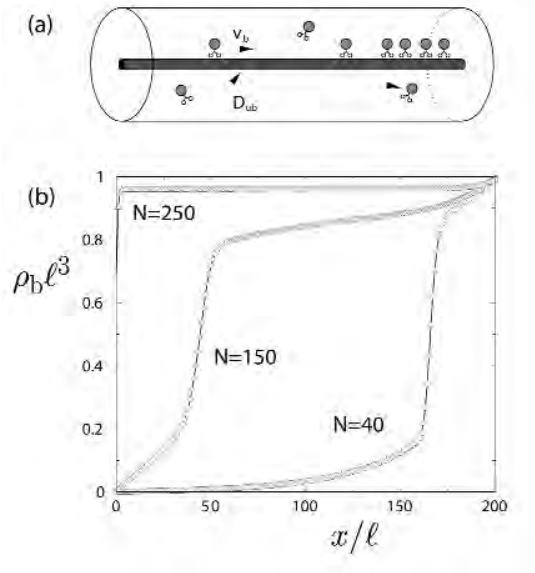

Fig. 3: (a) Motors move in a closed tube system which contains one filament and build up a motor traffic jam at the right end of the system. (b) Profiles of the bound motor density along the filament for various total numbers N of motors within the tube. The jammed region becomes longer with increasing N.

In closed tubes, the motors generate non-uniform density patterns and accumulate at the end of the tubes as shown in **Fig. 3**. The average bound motor current in these systems exhibits a maximum as a function of the motor concentration within the tube **[1]**.

Open tube systems, which are coupled to motor reservoirs at both ends, exhibit boundary-induced phase transitions **[3]**. The motor density within the tube is determined by the 'bottleneck' of the transport through the tube, which can be given by one of the boundaries or by the interior of the tube. Phase transitions occur if the position of the 'bottleneck' changes when the motor densities in the boundary reservoirs are changed.

Bidirectional Motor Traffic

Each molecular motor moves either towards the plus- or towards the minus-end of the corresponding filament, but different types of motors move into opposite directions along the same filament. In this situation, cooperative binding of the motors to the filament—in such a fashion that a motor is more likely to bind next to a bound motor moving in the same direction and less likely to bind next to a motor with opposite directionality—leads to spontaneous symmetry breaking **[4]**: For sufficiently strong motor-motor interactions, one motor species occupies the filament, while the other one is largely excluded from it as shown in **Fig. 4**. If several filaments are aligned in parallel and with the same orientation, this symmetry breaking leads to the spontaneous formation of traffic lanes for motor traffic with opposite directionality **[4]**.

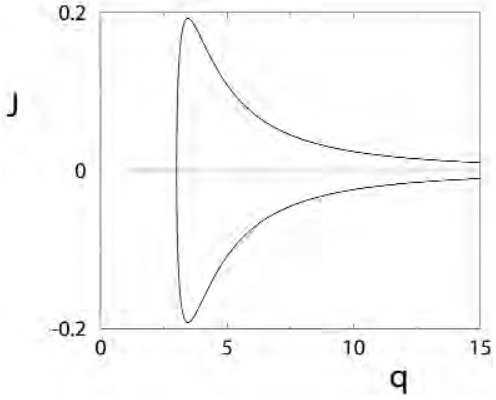

Fig. 4: Spontaneous symmetry breaking in systems with two motor species moving into opposite directions along the same filament: The total motor current J is zero for weak interaction $q<q_c$, where the filament is equally populated by both motor species, but non-zero for sufficiently strong motor-motor interactions with $q>q_c$, where one motor species is essentially excluded from the filament. For very strong interaction, the current decreases because the filament becomes more and more crowded.

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Protein Folding

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Since their discovery about 10 years ago, two-state folders constitute a new paradigm in protein folding. Two-state folders are proteins that fold from the denatured state to the native state highly cooperatively, without experimentally detectable intermediate states. Most of the small single-domain proteins characterized to date fold with two-state kinetics. These single domains are also thought to build the folding units of the larger and more complex multi-domain proteins.

The central experimental tool for investigating the folding kinetics of two-state proteins is mutational analysis. A careful mutational analysis requires generating a large set of single-residue mutants of the considered protein. The impact of each of these mutations on the folding kinetics is then typically characterized by the Φ-value, defined as

$$\Phi = \frac{RT \ln\left(k_{wt}/k_{mut}\right)}{\Delta G_N}$$

Here, k_{wt} and k_{mut} represent the folding rates of the wildtype and mutant of the protein, and ΔG_N is the change in stability induced by the mutation. The stability of a protein is the free energy difference between the denatured state D and the native state N.

Two-state folding is often described in transition-state theory, which assumes that the folding rate is proportional to $\exp(-G_T/RT)$. Here, G_T is the activation energy of the folding reaction, the free energy difference between the rate-limiting transition-state ensemble T and the denatured state D. This implies $\Phi=\Delta G_T/\Delta G_N$, which indicates that Φ-values measure the *energetic* consequences of mutations on the transition state ensemble relative to the native state.

A central question is whether Φ-values also contain *structural* information about the transition state ensemble. In the traditional interpretation, Φ=1 is taken to indicate that the mutated residue has native-like structure in the transition state ensemble, since the mutation-induced free energy shifts of the transition state ensemble and the native state, ΔG_T and ΔG_N, are equal. Oppositely, Φ=0 is taken to indicate that the mutated residue is not structured in the transition-state ensemble. Most of the mutations have 'fractional' Φ-values between 0 and 1, which apparently indicates a partially native-like structural character of the mutated residue in the transition state ensemble. However, there are several problems with this traditional structural interpretation. For example, Φ-values are sometimes 'nonclassical', i.e. they can be less than zero or larger than one. In the traditional view, such values cannot be interpreted.

We have recently developed a more rigorous interpretation of Φ-values **[5]**. In this interpretation, Φ-values have both *structural and energetic* components. The interpretation is based on a statistical-mechanical model that focuses on the formation of characteristic protein substructures during folding. The model describes the folding kinetics *via* a master equation which can be solved exactly **[3,5]**. In the model, Φ-values for mutations in an α-helical substructure with intrinsic stability G_α have the general form

$$\Phi = \chi_\alpha \frac{\Delta G_\alpha}{\Delta G_N}$$

Here, χ_α is a *structural* term between 0 and 1, indicating to which extent the α-helix participates in the transition state ensemble. The *energetic* term $\Delta G_\alpha / \Delta G_N$ can attain any value and can thus lead to nonclassical Φ-values smaller than 0 or larger than 1.

The protein CI2 (see **Fig. 1**) is one of the best-characterized two-state folders. The Φ-values for 20 single-residue mutations in the α-helix of CI2 range from –0.35 to 1.25. Our model reproduces these Φ-values with a correlation coefficient of 0.85, including several of the nonclassical Φ-values, and provides a consistent structural interpretation of these values **[5]**.

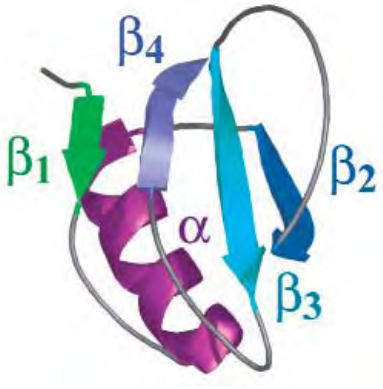

Fig 1: The protein CI2 is one of the best-characterized two-state folders. The structure of CI2 consists of an α-helix packed against a four-stranded β-sheet.

Another important question is why some proteins have *polarized* Φ-value distributions, while others have *diffuse* distributions. In a polarized distribution, the Φ-values in some of the secondary structural elements (helices or strands) of the protein are significantly larger than in other secondary elements. In a diffuse distribution, the average Φ-values for the secondary structural elements of the protein are rather similar.

We have found that the shape of many Φ-value distributions can be understood from loop-closure events during folding **[1, 2, 4]**. The loops of the protein chain closed during folding depend on the sequences of events in which the structural elements are formed (see **Fig. 2**).

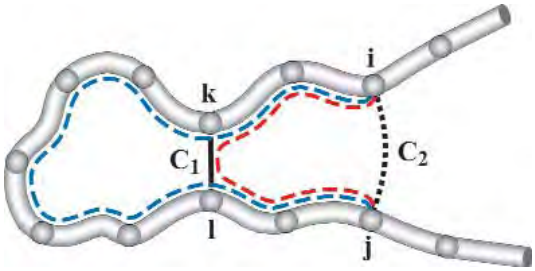

Fig. 2: Loop-closure dependencies between contacts. Forming contact C_2 prior to C_1 requires the closure of a relatively large loop (blue line). But if the contact C_1 closes first, the loop for forming C_2 is significantly smaller (red line).

On the minimum-entropy-loss routes of our models, the structural elements of the protein 'zip up' in a sequence of events that involves only relatively small loops (see **Fig. 3**). The 'kinetic impact' of the structural elements estimated from these routes correlates with the average experimental Φ-values **[4]**. A structural element that strongly affects the loop lengths for forming other structural elements is predicted to fold early and to have a high kinetic impact in this model.

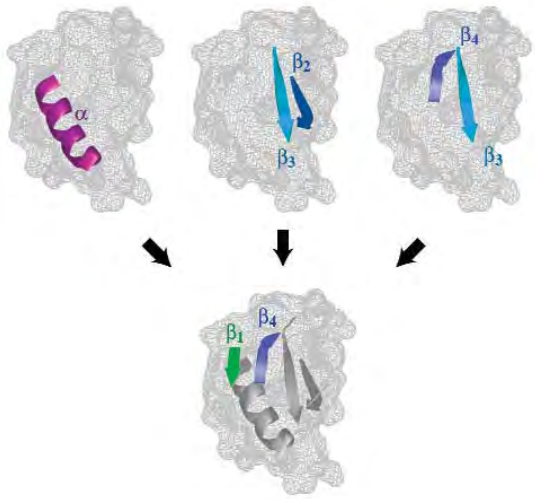

Fig. 3: Minimum-entropy-loss route for the protein CI2. Along this route, the nonlocal pairing of the terminal strands β_1 and β_4 is formed after the α-helix and after the local strand pairings $\beta_2\beta_3$ and $\beta_3\beta_4$. The prior formation of the three local structural elements reduces the length of the loop which has to be closed to form $\beta_1\beta_4$.

A third question currently addressed by us concerns the multiplicity of protein folding routes. According to the 'old view', proteins fold along well-defined sequential pathways, whereas the 'new view' sees protein folding as a highly parallel stochastic process on funnel-shaped energy landscapes. We have analyzed parallel and sequential processes on a large number of Molecular Dynamics unfolding trajectories for the protein CI2 at high temperatures **[6]**. Using statistical measures, we find that the degree of sequentiality depends on the structural level under consideration. On a coarse structural level of whole β-sheets and helices, unfolding is predominantly sequential. In contrast, the unfolding process is highly parallel on the level of individual contacts between the residues of the protein chain. On an intermediate structural level, the characteristic parallel and sequential events during unfolding can be understood from the loop-closure dependencies between the structural elements.

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Cellular Adhesion Clusters under Force

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Physical concepts are essential to understand the functioning of biological cells. For example, the physical properties of cytoskeleton, plasma membrane, adhesion clusters and extracellular matrix strongly influence cell shape, adhesion and migration, which in turn are essential elements of many important physiological processes, including development, inflammation and wound healing. During recent years, a large variety of new experimental tools has been developed in biophysics and materials science which now allow to characterize and control various physical determinants of cellular systems in a quantitative way. On the extracellular side, this includes the use of soft lithography to create biochemically, topographically and mechanically structured surfaces. On the intracellular side, this includes a large variety of novel fluorescence probes, colloidal spectroscopy and microrheology. In parallel to these experimental advances, concepts from statistical mechanics and soft matter physics have been increasingly applied to cellular systems.

In cell adhesion, physical concepts like force and elasticity are particularly important. Cells adhere to each other and to the extracellular matrix through clusters of transmembrane adhesion receptors, which on the intracellular side usually couple to the cytoskeleton. Therefore they usually are under considerable mechanical load. For example, adherens junctions in cell-cell adhesion and focal adhesions in cell-matrix adhesion are mediated by receptors from the cadherin and integrin families, respectively, which both couple to the actin cytoskeleton. In some cases, cell adhesion is determined by the interplay between several receptor systems. One example is the way in which white blood cells, but also stem and cancer cells exit the blood flow, as depicted schematically in **Fig. 1**. In the initial stages, the white blood cells bind to the vessel walls through receptors from the selectin family. Because the selectin bonds break rapidly, the cells start to roll, with new bonds forming at the front and old ones breaking at the back. The main function of rolling adhesion is to slow down the cell in such a way that it can survey the vessel walls for exit signals. If these are present, firm adhesion through long-lived integrin receptors is activated, leading to arrest and subsequent extravasation from the blood vessel. Thus rolling adhesion is characterized by the interplay of selectin and integrin receptors, which both couple to the actin cytoskeleton.

The coupling of adhesion clusters to the cytoskeleton does not only provide structural integrity, it also allows the cell to regulate the internal state of the adhesion cluster by force. For example, it has been shown during recent years that focal adhesion act as mechanosensors, i.e. they convert force into intracellular signalling events **[1,2]**. Mechanical properties of the extracellular environment modulate the build-up of actomyosin-generated force at focal adhesions and therefore can be sensed by cells through force-mediated processes at focal adhesion. Based on this information, cells can for example decide how to position and orient in a mechanically anisotropic environment **[3,4]**.

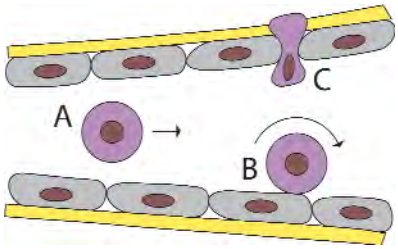

Fig. 1: White blood cells, but also stem and cancer cells travel the body in the blood flow (A). In order to exit the blood flow, they have to interact adhesively with the vessel walls. Initial adhesion is provided by short-lived selectin-bonds, resulting in rolling adhesion (B). Adhesion through long-lived integrin-bonds leads to firm arrest and extravasation (C).

Stochastic Dynamics of Adhesion Clusters

In order to understand these processes in more detail, microscopic models for force-modulated processes at adhesion clusters are required. In general, formation and rupture of adhesion bonds is a stochastic process. In this context, the simplest theoretical model for a biomolecular bond is a one-dimensional energy landscape with a transition state barrier separating the unbound from the bound state. Then the average bond lifetime T_0 can be identified with the mean first passage time to cross the transition state barrier. Kramers theory predicts that T_0 is an exponential function of barrier height in units of thermal energy. The resulting values for T_0 are typically of the order of seconds. Force tilts the energy landscape. For a sharp transition state barrier, Kramers theory predicts that average bond lifetime T under force decreases in an exponential way as function of force, $T = T_0 e^{-f}$, where f is force in units of thermal energy divided by the distance between the bound state and the sharp transition state barrier. The resulting intrinsic force scale typically is of the order of pico-Newtons. In 1978, Bell postulated this relation for single bonds under constant force. In 1997, Evans and Ritchie applied this concept to single bonds under time-dependent forces. They predicted that for a linearly rising force, average bond lifetime becomes a logarithmic function of loading rate. This prediction has been confirmed impressively in subsequent experiments and defined the new field of *dynamic force spectroscopy*. Since force is usually applied through some soft transducer, the bond cannot rebind after rupture due to elastic recoil of the transducer.

Since adhesion bonds in cellular systems usually act in a cooperative way in adhesion clusters, this single molecule effort now has to be extended to multiple bonds. In contrast to the situation with single bonds, now rebinding should be possible as long as at least one closed bonds can ensure spatial proximity of receptors and ligands. In order to investigate the role of force for the stochastic dynamics of adhesion clusters, we studied a one-step master equation for the dynamics of N parallel adhesion bonds under dimensionless force f and with dimensionless rebinding rate γ **[5,6]**. **Fig. 2** schematically shows the situation under consideration. In our model, we neglect spatial aspects and the state of the adhesion cluster is described completely by the number i of closed bonds. There are N+1 possible states ($0 \leq i \leq N$) and the

reverse and forward rates between the different state are $i\, e^{f/i}$ and $\gamma(N-i)$. Here the factor f/i reflects the fact that force is assumed to be shared equally between the closed bonds, leading to non-trivial cooperativity between the different bonds. For finite force, this model is highly non-linear and therefore difficult to solve. Nevertheless exact solutions can be found for several special cases, including f=0, γ=0 and N=2. In the general case of arbitrary N, f and γ, the master equation can be solved by computer simulations, for example by adapting the Gillespie algorithm for exact stochastic simulations. Computer simulations are also essential to reveal the nature of single rupture trajectories. For most of the time, these trajectories follow the smooth time course of the first moment. The final stages of rupture however are characterized by rather abrupt decay which results from the Arrhenius factor $e^{f/i}$ in the reverse rate: if the number of closed bonds i fluctuates to a smaller value, force on the remaining closed bonds and therefore their dissociation rate increase, leading to a positive feedback loop for rupture. Our analysis also shows that there is a threshold in force beyond which rupture is increased strongly. Moreover our master equation can be used to study the case of a linearly rising force **[7]**, a situation which is relevant for dynamic force spectroscopy on adhesion clusters.

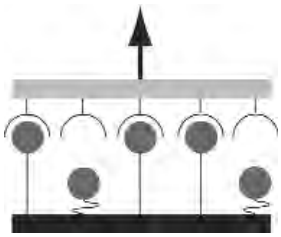

Fig. 2: Schematic representation of an adhesion cluster under force: in this cartoon, there are N=5 identical receptor-ligand bonds, of which i=3 are closed and equally share the dimensionless force f. At the same time, N-i=2 bonds are open and can rebind with the dimensionless rebinding rate γ.

For experimental purposes, the quantity of largest interest is the average cluster lifetime T as a function of the model parameters N, f and γ. This quantity can be identified with the mean first passage time to reach the completely dissociated state. For constant force, it can be calculated exactly from the adjoint master equation for arbitrary model parameters. In the case N=2, we find

$$T = \frac{T_0}{2}\left(e^{-f/2} + 2e^{-f} + \gamma e^{-3f/2}\right).$$

This two-bond equation can be understood as the generalization of Bell's single bond equation $T = T_0\, e^{-f}$. For arbitrary N, we find that average cluster lifetime T is always exponentially suppressed by force f and that the stabilizing contribution due to rebinding is a polynomial in γ of rank N-1.

Adhesion Clusters in Rolling Adhesion

In a collaboration with immunologists from the Weizmann Institute in Israel, we used these results to evaluate flow chamber data for white blood cells adhering under shear flow **[8,9]**. The red line with circles in **Fig. 3** shows the measured dissociation rate as a function of shear rate for single cells transiently tethered to the bottom of the flow chamber sparsely coated with ligands for L-selectin. At low shear, the dissociation rate plateaus at a value of 250 Hz, which most likely is the intrinsic dissociation rate of single L-selectin bonds. The force acting on the cell due to viscous drag from the hydrodynamic flow can be calculated from the Stokes equation. Combined with Bell's equation, this leads to the light blue line in **Fig. 3**, which clearly does not agree with the experimental data. However, this calculation neglects the fact that at low shear, both intrinsic dissociation and loading occur on the same time scale of milliseconds. Correcting Bell's equation for initially linear loading leads to the green line in **Fig. 3**, which is much closer to the experimental result. Most importantly, **Fig. 3** shows that at a shear rate of 40 Hz, the cellular dissociation rate suddenly drops by a factor of 14. This dramatic stabilization can be argued to result from multiple bond formation due to increased transport at higher shear. Several lines of reasoning suggest that the dominating event is the formation of two-bond clusters. The dark blue lines in **Fig. 3** are plots of the two-bond equation for different values for the rebinding rate γ. The value γ=40 (10^4 Hz in dimensional units) agrees best with the experimental data, suggesting that L-selectin mediated tethering in shear flow is characterized by unusual fast rebinding. Although these results represent only a small step toward a complete understanding of the complicated process of rolling adhesion, they show how quantitative evaluation of experimental data can help to dissect complex cellular systems.

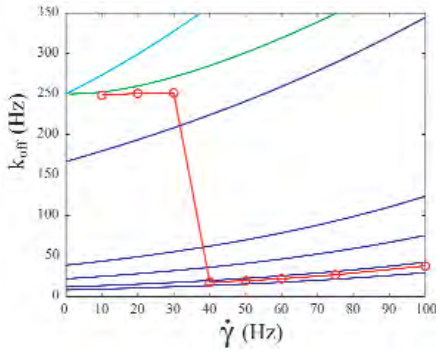

Fig. 3: Red line with circles: experimental data for cellular dissociation rate as a function of shear rate as measured in flow chambers for white blood cells adhering through L-selectin. Light blue line: single bond dissociation as predicted by Bell's equation with immediate loading. Green line: Bell's equation corrected for finite loading rate. Dark blue lines: two-bond equation for different values of the rebinding rate γ (γ=0, 10, 20, 40 and 60 from top to bottom). Agreement with the experimental data is best for γ=40.

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Evolution in Stochastic Environments

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Most environments in which life evolves have a stochastic nature. A particularly important element of stochasticity is produced by variations over time of the availability of the resources necessary to growth and reproduction.

For instance, parasites need a host that carries them around in order to get in contact and infect another, healthy, host. If the density of the hosts is very small, the encounters between hosts may be very rare and, from the point of view of the parasite, rather unpredictable. The parasites must therefore adapt to these conditions in order to avoid that all sick hosts die or get immunized before infecting a healthy one. One case study is given by the adaptation of the virus zoster, responsible for varicella, to the dynamics of early human groups **[1]**. In order to cope with the rare encounters between individuals in sparse populations, this virus has developed a mechanism that allows it to remain latent and inactive within the host after the varicella infection. The later outbreak in form of shingles is a strategy that increases the probability of propagation of the virus and thus enhances its fitness.

Another example is provided by organisms in extreme seasonal environments, where the conditions for growth and reproduction vary strongly from season to season. A much studied case of this kind are plants in deserts. In this environment, the conditions for life are restricted to a few months during winter and the yield, i.e. the number of seeds produced by each plant, may vary very much from season to season so that even zero yields can occur during some seasons. To adapt to such an environment, these species have developed two mechanisms. On the one hand, at the end of the season, the individuals devote all their energy to the production of their seeds and die afterwards. For this reason, they are called annual species. On the other hand, the seeds have a form of dormancy that allows them to germinate only with a certain probability $g<1$ even if the conditions for germination are met at the beginning of the next season. In this way, dormancy is a strategy that mantains a permanent soil seed bank and allows local populations to avoid extinction after seasons without yield **[2]**.

My research has mostly to do with the strategy of seed dormancy. Nevertheless, the methods used, a mixture of stochastic modelling and evolutionary game theory, can be applied to a much broader range of biological problems. In particular, these methods are useful to study evolution under conditions in which the revenue of a certain investment is dependent on external factors which vary strongly and are unpredictable. Presumably, such conditions were also prevalent when the early forms of life had to develop before any kind of homeostasis had emerged.

One important topic of theoretical population biology is to characterize the phenotypes that we would expect on the basis of evolution. In the case of dormant seeds, the phenotype is the fraction g of seeds in the seed bank that should germinate at the beginning of each season.

If the plants cannot predict how good or bad a season will be, they have two simple choices: all seeds germinate, i.e. $g=1$; or all seeds stay dormant, i.e. $g=0$. These two choices are called pure strategies in game theory. To find out whether evolution leads to one of the two pure strategies or to a mixed strategy, i.e. to $0<g<1$, one implements a method called invasibility analysis. The implementation of the method depends on the particular model for the population dynamics. Its main ingredient is to determine whether a small population playing the strategy g' can invade an environment dominated by a large population playing the strategy g. By means of both analytical and numerical techniques **[3]**, this method allows to compute the strategy g^* which survives attempts of invasion by any other strategy. The strategy g^* is then called the evolutionary stable strategy of the system. This means that evolution should lead to the phenotype g^*.

The analysis of how the evolutionary stable strategy g^* depends on other parameters, provides important information about the effect of these parameters on the evolutionary history of the species. In the case of seed dormancy, such parameters are given by the properties of the stochastic variable yield per season.

A particular issue that interested Prof. Katja Tielbörger, a plant ecologist at the University of Tübingen, and myself was the analysis of the evolutionary stable strategy when the seed bank is structured.

An obvious reason for why the seed bank is structured, is that there are seeds of several ages in the soil. If we consider each age as a class, then the seed bank is structured in age classes. From empirical studies on seeds, we know that several mechanical and biochemical processes are at work that have an effect on the germination properties of the seeds. We also know that these effects depend on time and therefore on age. This leads to the expectation that old viable seeds will react differently than younger seeds to optimal germination conditions. In particular, we would intuitively expect that older seeds have a higher germination probability than younger seeds. However, no theoretical studies exist to determine which changes of g we should expect to observe from the point of view of evolution.

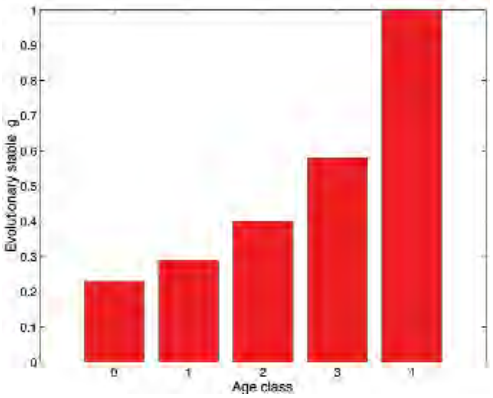

Fig. 1: The evolutionary stable strategy for structured seed banks is that older seeds (right) have higher germination probability than younger seeds (left).

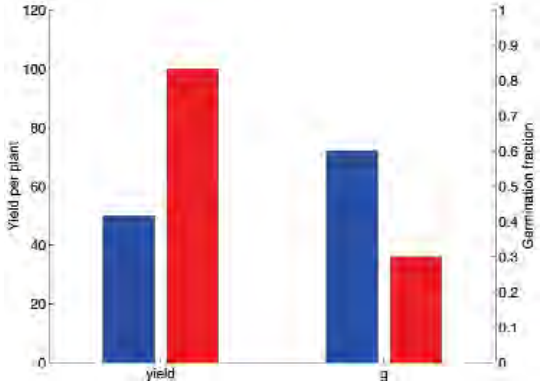

Fig. 2: Seeds from a bad season (blue) have a larger germination probability than seeds from a good season (red).

We have therefore developed and studied an evolutionary model to follow the evolution of g with the age of the seeds. The main result of the model is that the age-dependent g^* will grow with the age of the seeds **(Fig. 1)**. This result is in agreement with the intuitive expectation. It tells also that there must be an adaptation to the mechanical and biochemical mechanisms which influence the germination behaviour.

Another, less obvious structure became clear from several empirical studies. It was noticed that several plant species in several distinct locations produce seeds, which have a low germination probability after a very good season with large yield, and seeds with a large germination probability after a very bad season with small yield **(Fig. 2)**.

Until recently, the theoretical explanation for this empirical observation was based on the idea that the fitness of the plant is increased by decreasing the competition among siblings. This explanation, however, is valid only under particular competition conditions and in the absence of any stochasticity.

We have developed a different evolutionary model where we made the simplifying assumption that there are only two kinds of seasons, good and bad ones. In this way, we could structure the seed bank into two classes: seeds from good seasons and seeds from bad seasons. Our analysis shows that it is evolutionary convenient that seeds from good seasons have a lower germination probability than those from bad seasons.

Given the very general assumptions of the model, we concluded that this behaviour should be common to all annual species with permanent soil seed banks **[4]**.

I plan to apply this approach to other systems where evolution through competition between different strategies is believed to play an important role.

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Advanced Confocal Microscopy

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1999: PhD, Physical Chemistry (Bordeaux University, France) Thesis: Hydrodynamical Properties of Model Membranes Studied by Means of Optical Trapping Manipulation of Micron-Sized Particles
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The development of laser scanning microscopy has initiated a revolution in the investigation of the spatial structure of microscopic samples. In the last few years confocal microscopes have been improved to accommodate modern techniques like Fluorescence Correlation Spectroscopy (FCS) and Fluorescence Lifetime Image Microscopy (FLIM) thus furnishing the instruments with powerful tools.

FCS is a single molecule method for measuring concentrations and diffusion rates. Only molecules in the confocal volume are excited and detected via the emitted photons. This leads to intensity fluctuations as the molecules cross the confocal volume. FCS evaluates the fluctuations by determining the time dependence of the intensity correlation and by analyzing the time behavior of the fluctuations (see **Fig. 1**).

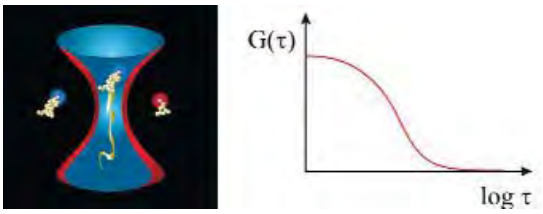

Fig. 1: FCS principle: Only molecules in the confocal volume are excited (left). The time correlation of the intensity spectrum (right) contains the information about the diffusion rates. The illustrations are reproduced from [1].

FLIM is based on time-correlated single photon counting technology. A multiphoton laser is used as excitation source (see **Fig. 2**). The instrument then records the fluorescence spectrum in all pixels of the image, thus allowing for efficient discrimination between different fluorescence markers. This leads to high contrast fluorescence imaging, enhanced depth resolution, less autofluorescence, and less photobleaching outside the focus. In contrast to intensity imagining, FLIM is insensitive to fluctuations in fluorochrome concentration and excitation light intensity.

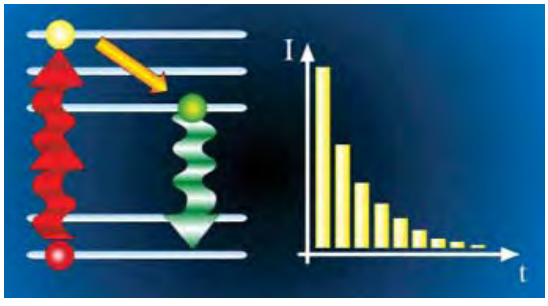

Fig. 2: FLIM principle: After 2-photon excitation (left) the fluorescence decay (right) in each pixel of the image is detected. The illustration is reproduced from [1].

The MPI-KG has recently received additional funding from MPG to install such a confocal microscope equipped with FCS and FLIM. A number of projects involving this microscope will be pursued:

Domains in Membranes (Theory Department):
Giant unilamellar vesicles made of lipid mixtures will be used as a model system to study domain formation in lipid bilayers. The different domains can be visualized by fluorescent probes which preferably partition in one of the phases. Using FCS the local fluidity of the membrane can be probed. As an extension to the confocal microscope setup, we intend to adapt a micropipette system. The micropipettes would allow for manipulation and spatially fixing the vesicle under study. In addition, applying some suction pressure with a pipette induces tension on the aspirated vesicle. We intend to study the effect of membrane tension on the morphology and behavior of the phase separation and domain formation in the lipid bilayer.

Fusion of Model Membranes (Theory Department):
As a model system, we use giant vesicles. Two ways of inducing fusion will be investigated: (i) Membranes functionalized with fusogenic molecules are brought together by means of micropipettes and exposed to a solution of trivalent metal ions. The latter make a fluorescently active coordination complex with fusogenic molecules from opposing bilayers. Thus the membranes are brought together and fuse. (ii) When subjected to short square-wave electric pulses vesicles porate. If two vesicles are close together, they fuse when subjected to the pulse. The fusion of vesicles can be partial consisting of hemifusion where only the external leaflets of the membranes fuse, or complete where the internal volumes of the two vesicles mix. In order to distinguish between the two cases we intend to study fusion on vesicle couples where one of the vesicles is fluorescently labeled and the other is not labeled. Another aspect of this project is related to fusing vesicles of different membrane composition which would lead to constructing membranes with two microdomains. To resolve the dynamics of the fusion process we intend to use FLIM.

Cells on Artificial 3D Scaffolds (Department of Biomaterials):
Here the main purpose of using confocal microscopy is to analyze cells grown on 2D and 3D scaffolds. In order to test different hydroxyapatite materials for their biocompatibility, 3D scaffolds will be seeded with osteoblast-like cells. These cells start forming a tissue-like network from collagen within the holes of the scaffold material. It is an advantage to get a 3D reconstruction from the behavior of the cells in the pores in order to learn how the process of an extracellular matrix formation by osteoblasts develops. The high resolution that a confocal microscope equipped with FLIM allows would also provide the possibility to visualize intracellular structures of the cells to observe changes and reorganization of the cytoskeleton. Depth projection analysis is useful to observe the cells in the porous network. Moreover, the morphology of the cells and the dynamics of their behavior on membranes and stretched membranes can be analyzed.

Microporous Materials for Structural and Electronic Purposes (Department of Colloid Chemistry):
Modern sensing material, solar cells, actuators and catalysts, but also high performance insulating foams and porous construction materials possess a hierarchical pore structure with voids from the nanometer to the micron scale. Confocal microscopy, especially in a "chemical composition mode" (e.g. vibrational mode sensing), is one of the few techniques to characterize texture and structure of such foams (of transparent or thin opaque materials). The requirement for the confocal microscope is maximal resolution (blue laser), specimen penetration, and chemical analysis in the detection.

Selective Permeation of Dyes through Films and Membranes (Department of Interfaces):
A new type of microcapsules with walls of controlled thickness in the nm range and of designed composition (polyelectrolytes, inorganic particles, proteins) has been developed that, in addition, has been coated by a lipid bilayer. Qualitatively, it has been shown that the permeation of macromolecules as well as ions can be switched via pH, salt, light or electromagnetic pulses. The permeation can be followed by time dependent microfluorescence with dye labeled molecules following a bleaching pulse. For an in-depth understanding and control of the properties it is mandatory to systematically vary molecular parameters (size, shape, hydrophilicity, charge) of the permeant, the shell material, and preparation conditions. The experimental requirements are time resolution into the range of seconds, high sensitivity and dynamic range.

Dynamics of Dyes in Polymeric Gels (Department of Interfaces):
Dyes and drugs can be concentration enriched within gels in capsules and then be released by changes of pH, temperature or solvent. The dynamics within these gels is largely unknown. From fluorescence lifetime imaging, we expect to deduce information on the fraction of free dyes and those bound to the matrix. From FCS with polarized emission we expect information on the local dynamics of optical probes. This is of special interest for systems undergoing sol/gel transitions which macroscopically resemble first-order phase transitions, but where the local dynamics remains to be elucidated.

Folding of Polypeptides at Membranes and at Interfaces (Department of Interfaces):
Hydrophobic surfaces have been shown to inhibit the β-sheet formation of the rather small peptide β-Amyloid. Understanding this process is of utmost importance to prohibit diseases like Alzheimer's. The measurement of secondary structure changes is usually based on circular dichroism and Fourier transform infrared spectroscopy but this is very difficult for monolayers. In particular, the kinetics of folding by fluorescence resonance energy transfer will be studied. For this purpose peptides will be labeled by donor and acceptor dyes and particles of hydrophobic and hydrophilic surfaces will be prepared to compare the kinetics.

Emission of Spherical Shells as Optical Resonators (Department of Interfaces):
It is possible to dope polyelectrolyte shells by organic dyes and luminescent semiconductor quantum dots such that the radial position is defined with precision better than 5 nm. This is expected to give rise to so-called "Whispering gallery modes", a narrow optical emission with peaks depending on the precise geometry. The existence of these modes shall be proved by local spectroscopy (in particular FLIM) with individual shells and the properties will be tested in light of recent theories.

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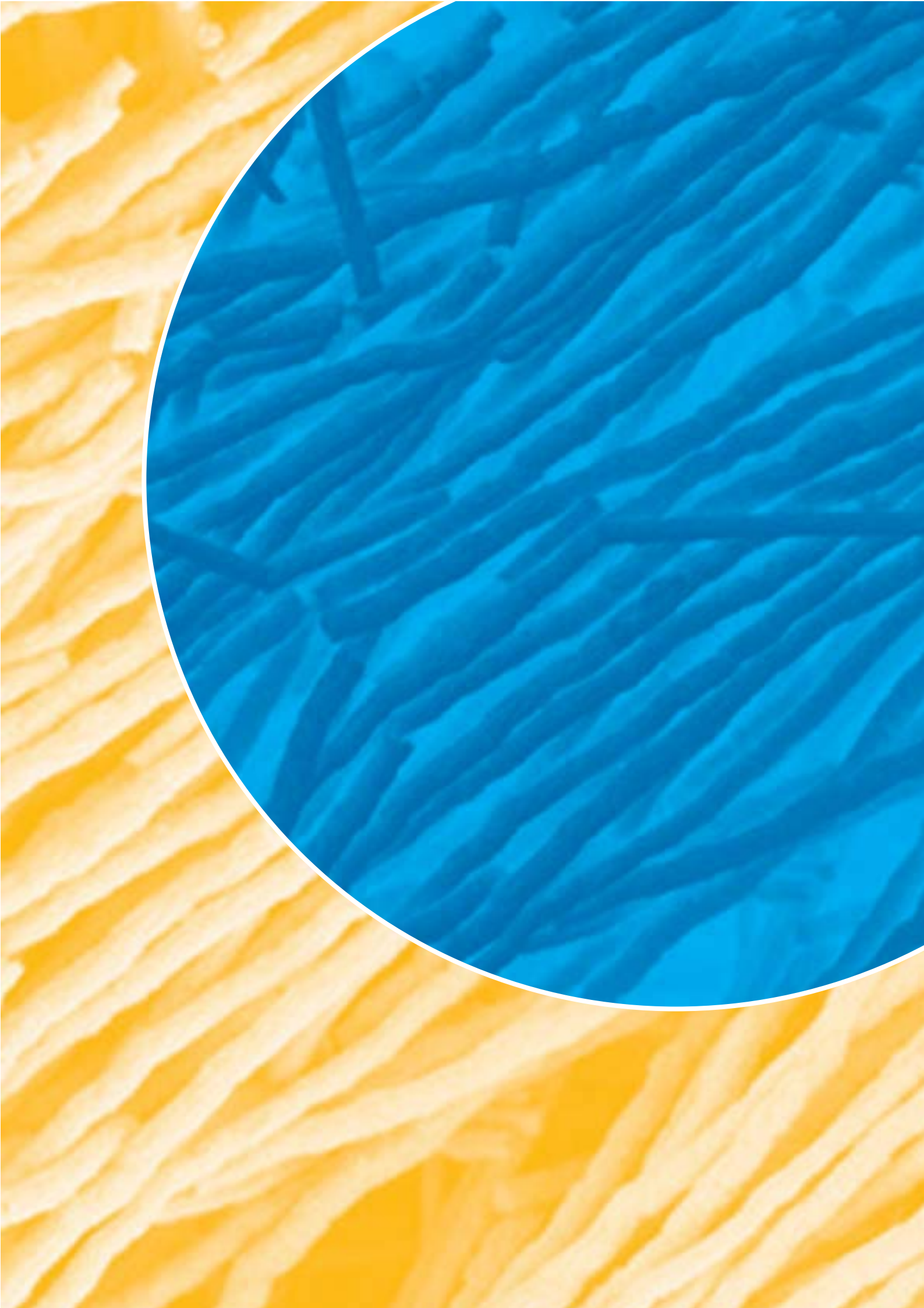
References:
[1] www.confocal-microscopy.com/website/sc_llt.nsf

APPENDIX

APPENDIX APPENDIX APPENDIX



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BMBF	Selbststrukturierende organisch-anorganische Hybridnanopartikel auf der Basis von amphiphilen Blockcopolymeren und Charakterisierung des Bildungsmechanismus ihrer Überstrukturen	Dr. Cölfen KC	01.06.2001-30.04.2004	Forschungszentrum Jülich GmbH
BMBF	Weiterentwicklung und Betrieb der Messstrecken A2 und BW4 für Kleinwinkelstreuung am HASYLAB (DESY)	Dr. Fenzl GF/TH	01.04.2001-31.03.2004	
BMBF	Nanobiotechnologie-Verbundprojekt: Multifunktionale künstliche Zellen als Transporter, Sensoren und Nanoreaktoren	Dr. Sukhorukov GF	01.05.2002-30.04.2005	Universität Leipzig Capsulution Nanoscience AG
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BMWi	Innovationskompetenz mittelständischer Unternehmen: Ausarbeitung der konzeptionellen Idee und Testung der Entwicklungsstufen zur Entwicklung eines allgemein anwendbaren Gerätes zur Bestimmung der physiko-chemischen Stabilitätsparameter von Schaum	Dr. Lunkenheimer UG	06.03.2002-28.02.2004	GIT Gesellschaft für innovative Technologie mbH
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TH – Abteilung Theorie/Department of Theory
UG –Unabhängige Gruppe/Independent Research Group

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DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Biomimetische Mineralisation mit amphiphilen Blockcopolymeren	Dr. Cölfen KC	01.01.1998-31.12.2003	
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbund-systeme; Synthese und Untersuchung des Assoziationsverhaltens von neuen linearen und verzweigten amphiphilen Blockcopolymeren	Dr. Schlaad KC	01.01.1998-31.12.2003	
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbund-systeme; Phasenverhalten reiner Stoffe und binärer Mischungen in geordneten mesoporösen Materialien	Prof. Antonietti KC	01.01.1998-31.12.2003	
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Wechselwirkung von Nanopartikeln und Membranen	Prof. Lipowsky Dr. Döbereiner TH	01.01.1998-31.12.2003	
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbund-systeme; Elektronentransferreaktionen in Materialien mit Polaritätsgradienten	Prof. Möhwald GF	01.01.1998-31.12.2003	Universität Potsdam
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Hierarchische Architekturen aus Modulen mit metallosupramolekularen Koordinations-Polyelektrolyten	Prof. Möhwald Dr. Kurth GF	01.01.2001-	
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Strukturbildung und Dynamik in selbstorganisierenden Blockcopolymer-Tensid-Mischsystemen	Dr. Schlaad KC	01.01.2004-	TU Berlin
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Ordnungsstrukturen in Systemen aus stäbchenförmigen Molekülen	Prof. Lipowsky Dr. Gruhn TH	01.01.2004-	
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Synthese molekularer Objekte mit neuer Architektur und deren hierarchische Strukturbildung	Prof. Antonietti KC	01.01.2004-	FU Berlin
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Strukturbildung von Polyelektrolyten und Kolloiden an flüssigen Grenzflächen und in dünnen Filmen	Prof. v. Klitzing GF	01.01.2004-	
DFG/TU Berlin	SFB 448: Mesoskopisch strukturierte Verbundsysteme; Molekulare Prozesse in mesoskopisch strukturierten Polyelektrolytsystemen	Prof. Möhwald GF	01.01.2004-	TU Berlin

Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Magnetische Eigenschaften, Strukturbildung und Synthese von Submikrometer großen magnetischen Hohlkugeln	Dr. Caruso GF	01.12.2001-31.05.2003	
DFG	Photonic Crystals from Coated Colloids	Dr. Caruso GF	01.08.2001-31.07.2003	
DFG	Kombination von Reflektions-Interferenz-Kontrast-Mikroskopie mit kraftmikroskopischen Methoden zur Untersuchung von Adhäsion und mechanischen Eigenschaften von Polyelektrolyt- Hohlkörpern	Dr. Fery GF	01.05.2003-30.04.2005	
DFG	Enzymatisch gesteuerte Benetzungsübergänge in zweidimensionalen dipolaren Langmuir-Filmen	Dr. Fischer GF	01.09.2002-31.10.2004	
DFG	Untersuchung und Charakterisierung supramolekularer Aggregate	Dr. Kurth GF	01.12.2002-30.06.2004	
DFG	Molekulare Orientierung und Aggregation von Tensiden an Grenzflächen zwischen zwei Flüssigkeiten	Dr. Miller GF	01.10.2002-30.09.2004	
DFG	Der Zusammenhang zwischen der Stabilität von Schäumen und Emulsionen und der Änderung der freien Energie bei der Bildung dünner Flüssigkeitsfilme	Dr. Müller GF	01.11.2000-31.05.2003	
DFG	Bildung zwei-dimensionaler hoch organisierter Strukturen auf Basis komplementärer Wasserstoffbrückenbindungen durch molekular-spezifische Erkennung	Prof. Vollhardt GF	26.11.2001-31.12.2003	
DFG	Auto-Oszillationen der Oberflächenspannung: Mechanismus und Wirkungsprinzipien eines neuartigen selbstorganisierenden dissipativen Systems	Prof. Vollhardt GF	15.05.2001-14.05.2003	
DFG	Controlled Radical Polymerization	Dr. Tauer KC	01.11.2002-14.12.2004	
DFG	Kolloidale magnetische Flüssigkeiten: Grundlagen, Entwicklung und Anwendung neuartiger Ferrofluide	Dr. Landfester KC	15.07.2001-26.04.2003	
DFG	Biokompatible magnetische Partikel: Herstellung und Charakterisierung polymerverkapselter, super-paramagnetischer Nanopartikel	Dr. Landfester KC	01.08.2002-30.09.2003	
DFG	Fluktuierende Riesenvesikel als morphologische Sonden zur Untersuchung der Materialeigen-schaften amphiphiler Membranen und ihrer Wechselwirkung mit biologischen Makromolekülen	Dr. Döbereiner TH	01.05.2001-30.042003	

Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Adhäsion von Vesikeln an lateral strukturierten Grenzflächen	Prof. Lipowsky TH	01.05.2002-30.04.2004	
DFG	Simulation von an einer Fest-Flüssig-Grenzfläche verankerten Polyelektrolytketten bei expliziter Behandlung von Gegen- und Salzionen	Dr. Seidel TH	01.08.2001-31.07.2003	
DFG	Untersuchung der spezifischen Wechselwirkung maßgeschneiderter Blockcopolymere und Polypeptide mit Mineraloberflächen in AFM-Desorptionsmessungen	Dr. Cölfen KC	01.11.2003-	
DFG	Kristallisation von Calciumcarbonat und -phosphat über mesoskopische Transformation von Precursorpartikeln in natürlichen organischen Matrizen als Template und Modellsysteme für Biomaterialien	Dr. Cölfen KC	15.10.2003-14.10.2005	
DFG	Entwicklung von katalytisch aktiven Dendrizymen mit enzymanalogem Struktur-Wirkungsprofil	Dr. Kurth GF	15.07.2004-14.07.2005	
DFG	Structure Elucidation of Shear Oriented Ionic Self-Assembled Materials (SISAM)	Prof. Antonietti KC	09.09.2003-	
DFG	Higher Levels of Self-Assembly of Ionic Amphiphilic Copolymers: Strategies Based on Multiple Molecular Interactions (SONS-AMPHI)	Dr. Schlaad KC	01.10.2003-30.09.2005	
DFG	Auto-Oszillationen der Oberflächenspannung: Mechanismus und Wirkungsprinzipien eines neuartigen selbstorganisierenden dissipativen Systems	Prof. Vollhardt GF	15.05.2003-31.07.2004	
DFG	Counterion distribution in aligned lamellar phases and on monolayers at the air/water interface	Prof. Möhwald GF	01.11.2004-	
DFG	Adhesion and Fusion of Model Lipid Membranes	Dr. Dimova TH	01.01.2004-	
DFG	Controlled Precipitation of Biominerals using Catanionic Surfactant Self- Assembly Structures	Dr. Cölfen KC	15.08.2004-	

Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Koordinationsfonds des deutsch-französischen Kooperationspakets: Complex fluids: From 3 to 2 Dimensions	Prof. Möhwald GF	01.01.2004-31.12.2005	
DFG	Adsorptionsdynamik von Tensiden an Grenzflächen zwischen zwei Flüssigkeiten in Anwesenheit von Lösungsmittelgradienten.	Dr. Miller GF	01.10.2004-30.09.2006	
DFG	Nanodrähte und Nanoröhren: von kontrollierter Synthese zur Funktion	Dr. Niederberger KC	15.07.2004-14.07.2006	
DFG	Controlled Radical Polymerization (CRP) in aqueous heterophase systems	Dr. Tauer KC	01.11.2004-	
DFG	Funktionalisierte Monoschichten auf der Basis oberflächenaktiver Stoffe und polymerer Verbindungen	Dr. Miller GF	22.03.2002-	
DFG	Amyloid-Lipid-Wechselwirkung an Grenzflächen	Dr. Brezesinski GF	01.03.2003-28.02.2005	
DFG	Struktur metallosupramolekularer, hierarchisch strukturierter Materialien mit periodisch geordneten Metall-Ligand-Komplexen	Dr. Kurth GF	01.06.2003-31.05.2005	
DFG	Emmy-Noether-Programm: Modelling forces and signalling in cell adhesion – Nachwuchsgruppe	Dr. Schwarz TH	01.11.2001-31.10.2003	
DFG	Emmy-Noether-Programm: Bioorganische und biomimetische Polymere: Synthese, Charakterisierung und Anwendung der Polymerhybridsysteme – Nachwuchsgruppe	Dr. Börner KC	01.02.2003-	
DFG	Emmy-Noether-Programm: Modelling forces and signalling in cell adhesion – Nachwuchsgruppe	Dr. Schwarz TH	01.01.2004-31.01.2005	
DAAD	Projektbezogener Personenaustausch mit Frankreich	Dr. Brezesinski GF	01.01.2003-31.12.2004	

EU

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
ESA/ESTEC	Topical Team: Foam and Emulsion Technologies- Concerted Action Team	Dr. Miller GF	01.10.2003-31.12.2004	Université Aix-Marseille Université Compiegne I.C.F.A.M. Genua
ESA/ESTEC	FASES - Fundamental and applied studies of emulsion stability	Dr. Miller GF	01.10.2003-30.09.2006	Universität Florenz
ESA	Bone Structure, changes in Microgravity	Dr. Saparin BM	01.10.2004-30.09.2005	Charité – Universitätsmedizin Berlin Universität Potsdam ZIB Berlin University of Aarhus Scanco Medical AG Siemens AG Indeed – Visual Concepts GmbH
EU	Nanocapsules with functionalized surfaces and walls	Prof. Möhwald GF	01.09.2000-31.08.2004	CNRS Toulouse EPFL-Dept. Chimie LCPPM, Lausanne I.C.F.A.M. Genua Advanced Drug Delivery Technologies AG Muttenz Nimbus Biotechnologie GmbH Leipzig, Faculdade Engenharia da Universidade do Porto, Porto, Universität für Bodenkultur, Wien
EU	Marie-Curie Programm “Early Stage Training on Biomimetic Systems”	Prof. Lipowsky Dr. Valleriani TH	01.09.2004-31.08.2005	University of Copenhagen Politecnico di Milano Université Paul Sabatier Toulouse University of Edinburgh University of Leoben
EU	Marie Curie Research Training Networks (RTN): Self-organized nanostructures of amphiphilic copolymers	Prof. Antonietti Dr. Schlaad KC	01.01.2004-31.12.2007	Universität Bayreuth, TU Berlin Wageningen Universiteit Commissariat a L’Energie Atomique, Paris Centre National de la Recherche Scientifique, Paris Univerzita Karlova v Praze BASF Aktiengesellschaft Rhodia Recherches S.A., Aubervilliers Universität Basel Moscow State University
EU	Nanocapsules for Targeted Controlled Delivery of Chemicals	Dr. Sukhorukov GF	01.03.2004-28.02.2007	SINTEF, Norwegen UFC, Frankreich ICSC, Poland PlasmaChem, Mainz Coventya, Frankreich Coatex, Frankreich ICB, Polen

Stiftungen

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
AvH-Stiftung	Sofja Kovalevskaja-Preis: Design of multifunctional micro- and nano-sized polymer capsules	Dr. Sukhorukov GF	01.12.2001-31.12.2005	
VW-Stiftung	Tunable Selfassembled 2D and 3D photonic band-gap structures for applications in the visible optic, infrared and mm-wave ranges	Prof. Möhwald Dr. Caruso GF	01.03.2000-28.02.2003	Hebrew University of Jerusalem
VW-Stiftung	Polyoxometalate clusters in self-assembling hierarchical architectures: from discrete nanoscopic structures to extended liquid crystalline mesophases	Dr. Kurth GF	01.09.2002-31.08.2005	Universität Bielefeld Humboldt-Universität zu Berlin
VW-Stiftung	Biocomposite capsules as artificial viruses	Dr. Brezesinski GF	01.01.2003-31.12.2005	Universität Leipzig Universität Bochum
VW-Stiftung	Nanoengineered polymer capsules: tools for detection, controlled delivery and site specific manipulation	Dr. Sukhorukov GF	01.07.2004-30.06.2007	Universität München Internationale Universität Bremen
VW-Stiftung	Blockcopolymer vesicles with controlled uptake/release functions for drugs and Genes	Prof. Antonietti KC	15.07.2004-14.07.2007	Universität Hamburg Universität Duisburg Universität Freiburg
ZEIT-Stiftung	Nanochemie für eine zukünftige Automobiltechnik	Prof. Antonietti KC	01.01.2001-31.12.2003	MPI für Chemische Physik fester Stoffe Fritz-Haber-Institut der Max-Planck-Gesellschaft MPI für Kohleforschung

Industrie

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
Bayer AG	Untersuchung des Adsorptionsverhaltens von Dispergierhilfsmitteln auf Oberflächen von organischen Feststoffteilchen	Dr. Miller Dr. Lunkenheimer GF/UG	01.07.2000-30.06.2003	
BASF AG	Polyurethandispersionen via Mini-Emulsionspolymerisation	Dr. Landfester KC	01.12.2000-30.11.2003	
BASF AG	Entwicklung neuer Detektionstechniken für die Analytische Ultrazentrifugation	Dr. Cölfen KC	01.12-2001-30.11.2004	
8sens.Bio-gnostic AG	Nanoverkapselte Enzymkristalle für Affinitätstests	Dr. Caruso GF	01.11.2001-31.10.2003	
Mitsubishi	Surface control by functional polymers	Prof. Antonietti Dr. Landfester KC	01.03.2002-28.02.2003	
L'Oréal	Nanocapsules and the encapsulation of lipophilic and hydrophilic molecules in particles composed of polyester type polymers by using the technology.	Prof. Antonietti KC	01.08.2002-31.07.2003	
AT&S	Kontrollierte Herstellung von Dispersionen leitfähiger Materialien	Prof. Antonietti KC	01.06.2002-31.05.2003	
Clariant AG	Entwicklung neuer Herstellungsverfahren zur Synthese und Verkapselung organischer Pigmente	Prof. Antonietti Dr. Landfester KC	01.06.2003-31.05.2004	
Clariant AG	Beeinflussung von Kristallisationsprozessen	Prof. Antonietti KC	01.10.2004-30.09.2005	
Schering AG	Kolloidale Diagnostika für die MRI	Prof. Antonietti KC	01.04.2004-30.03.2005	

Ausgewählte Veranstaltungen
Selected Events

- **09 April 2003 Poster Session**
  Price: Ilka Bischof and Ulrich Schwarz: "Cell Organization in Soft Media due to Active Mechanosensing"

- **06 May 2003 Campus Info Day**
  Surveys of Scientific Activities of the Golm Institutes and talks about more specific research topics

- **08 May 2003 Girl's Day**

- **12-13 May 2003 Soft Matters 2003**
  A Bilateral Symposium sponsored by the Laboratory for Research on the Structure of Matter (Philadelphia) and the Max Planck Institute of Colloids and Interfaces (Potsdam)

- **20 June 2003 Alumni Meeting and Poster Session**
  Trends in Colloids and Interface Science

- **05-10 October 2003 LB 10 on Organized Molecular Films in Beijing (China)**

- **12-13 November 2003 Meeting of the Scientific Committee/Fachbeirat and Poster Session**

- **26 November 2003 11th Anniversary of the Max Planck Institute of Colloids and Interfaces**

- **21 December 2003 Sonntagsvorlesung im Alten Rathaus Potsdam**
  "Auf die Verpackung kommt es an – Wirkstoffe in der Nano- und Biotechnologie" *Prof. Helmuth Möhwald*

- **22 April 2004 Girl's Day**

- **23 April 2004 International Max Planck Research School on "Biomimetic Systems" (IMPRS) – Symposium**

- **12 May 2004 Leibniz-Kolleg Potsdam: "Evolution in der Chemie"**
  Experimental demonstrations for teachers and pupils

- **13 May 2004 Leibniz-Kolleg Potsdam: "Evolution in der Chemie"**
  Vortrag: Evolution in der gezielten Molekülsynthese, Nobelpreisträger *Prof. Jean-Marie Lehn*
  Direktor ISIS, Universität Louis Pasteur, Straßburg

- **11 June 2004 Alumni Meeting and Poster Session**
  Trends in Colloids and Interface Science, Price: *Markus A. Hartmann* et al.: Trabecular Bone Remodelling

- **09-12 September 2004 6th Elba Max Planck Forum on Nanoscale Science and Technology**
  Synchrotron Radiation and Nanobiosciences, Porto Conte - Sardinia (Alghero), Italy

- **26-30 September 2004 International Engineering Conference on Micromechanical Properties of Biomaterials**
  Tomar, Portugal

- **07-08 October 2004 Kick-off Meeting of the Marie Curie – Early Stage Training on "Biomimetic Systems"**
  Max Planck Campus Potsdam

- **05 November 2004 Symposium zur Systembiologie**
  Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Max-Planck-Institut für Molekulare Pflanzenphysiologie
  Max-Planck-Campus Potsdam

- **17 November 2004 „Nanochemische Konzepte einer nachhaltigen Energieversorgung (ENERCHEM)"**
  Eröffnungskolloquium, München

- **22-23 November 2004 14th Ostwald-Kolloquium**
  "Fluids at Interfaces and in Pores: Phase Transitions and Related Phenomena" Tagungsstätte Harnack Haus, Berlin

- **17 December 2004 "Bionano – Zukunft der Nanotechnologie"**
  Berlin-Brandenburgische Akademie der Wissenschaften

Wissenschaftliche Abschlüsse
Scientific Degrees

Diploma Theses

Department of Interfaces:

Bodenthin, Y.: Struktur dünner Filme aus metallo-supramolekularen Modulen. Universität Potsdam 2003.

Dönch, I.: Rasterkraftmikroskopie und Polyelektrolyt-Multilagen. FU Berlin 2004.

Master Theses

Department of Biomaterials

Stachewicz, U.: Mechanical Mapping of Compact Bone with Lamellar Resolution. University of Applied Sciences Münster and AGH University of Science and Technology in Krakow 2004.

Department of Colloid Chemistry

Franke, D.: Towards insulated molecular wires: Polymerization of surface active monomers onto 1-D and 2-D supramolecular supports. Universität Potsdam 2003.

Ba, J.: The synthesis of macroporous polymer gels and their use as scaffolds for fuel cell membranes and catalysts. Universität Potsdam 2004.

Fischer, A.: Synthesis and Characterization of mesoporous crystalline tin oxide. Universität Paris 2004.

Sel, Ö.: Towards Functional Hierarchical Polymer Colloids. Universität Potsdam 2004.

PhD Theses

Department of Biomaterials

Wöß, A.: Rapid Prototyping zellulärer Materialien. University of Leoben 2004.

Department of Colloid Chemistry

Krasia, T.: Synthesis and colloidal properties of a novel type of block copolymers bearing β-dicarbonyl residues. Universität Potsdam 2003.

Montenegro, R.: Crystallization, Biomimetics and Semiconducting Polymers in Confined Systems. Universität Potsdam 2003.

Thomas, A.: Poröse Silikate durch Nanocasting: Von chiralen Templaten zu neuer Chemie in Poren. Universität Potsdam 2003.

Deshpande, A. S.: Synthesis of Porous Oxide for catalytic applications using templating techniques. Universität Potsdam 2004.

Erbe, A.: Ellipsometrische Lichtstreuung als neue Methode zur Charakterisierung der Grenzfläche von Kolloiden. Universität Potsdam 2004.

Losik, M.: Phasenverhalten von Polypeptid-Blockcopolymeren. Universität Potsdam 2004.

Lucas, G.: Gradientenzentrifugation: Neue Anwendungen eines klassischen Verfahrens. Universität Potsdam 2004.

Ramirez Rios, L. P.: Superpara- and paramagnetic polymer colloids by miniemulsion processes. Universität Potsdam 2004.

Sinn, C.: Ion binding to polymers and lipid membranes in aquenous solutions. Universität Potsdam 2004.

Taden, A. J.: Kristallisationsphänomene in Miniemulsionen: Geordnete Strukturen und Anwendungen für die Enzymatische Polymerisation. Universität Potsdam 2004.

Wohlrab, S.: Polymerinduzierte Morphogenese bei der Kristallisation von Aminosäuren. Universität Potsdam 2004.

Department of Interfaces:

Antipov, A. A.: Polyelectrolyte multilayer capsules as controlled permeability vehicles and catalyst carriers. Universität Potsdam 2003.

Bosio, V.: Interaction of multilayer coated surfaces studied by colloidal probe atomic force microscopy. Universität Potsdam 2003.

Heinig, P.: The Geometry of Interacting Liquid Domains in Langmuir Monolayers. Universität Potsdam 2003.

Ibarz-Ric, G.: Controlling internal structure and permeability of polyelectrolyte multilayer microcapsules. Universität Potsdam 2003.

Kraß, H.: Neuartige supramolekulare Polyoxometallat- und Polyelektrolyt-Amphiphil Komplexe. Universität Potsdam 2003.

Radtchenko, I. L.: Nanoengineered polymeric capsules as physico-chemical microreactors. Universität Potsdam 2003.

Schneider, M.: Untersuchung von Wechselwirkungskräften und dem Adsorptionsverhalten von Polyelektrolytmolekülen auf Nanometer-Skala. Universität Potsdam 2003.

Schöler, B.: Einfluss der Ladungsdichte auf den Aufbau von Polyelektrolyt Multischichten mit der Layer-by-Layer Technik. Universität Potsdam 2003.

Schollmeyer, H.: Zweidimensionale molekulare Ordnung und Strukturbildung: Triakontan an planaren SiO_2/Luft-Grenzflächen. Universität Potsdam 2003.

Schütz, P.: Dünne Kompositfilme aus Nanopartikeln und Polyelektrolyten. Universität Potsdam 2003.

Schwarz, B.: NMR Spektroskopie an Polyelektrolyt Mono- und Multischicht-Systemen. Universität Potsdam 2003.

Wang, L.: Lipid monolayers coupled to polyelectrolyte multilayers: Stability, dynamics and interactions. Universität Potsdam 2003.

Dong, W.-F.: Polyelectrolyte Multilayer Capsules: Structure, Encapsulation, and Optical Properties. Universität Potsdam 2004.

Li, L.: Polyelectrolyte Hollow Capsules Functionalized for Vectorial Electron Transfer. Universität Potsdam 2004.

Muruganathan, R.: Permeability and Interaction in Freestanding Foam Films. Universität Potsdam 2004.

Rusu, M.: Phase transitions of thermoreversible polymers in polyelectrolyte multilayers. Universität Potsdam 2004.

Sobal, N. S.: Kolloide Nanosysteme aus magnetischen und metallischen Materialien: Synthese und Charakterisierung. Universität Potsdam 2004.

Teixeiro Cordeiro, A. L.: Viscoelastic Nanocapsules under Flow in Microdevices. Universidade do Porto 2004.

Yue, X.: Monolayer Phase Behavior of Bipolar Amphiphiles and their coupling with DNA. Universität Potsdam 2004.

Theory Department:

Brinkmann, M.: Benetzung lateral strukturierter Oberflächen. Universität Potsdam 2003.

Franke, T.: Haftübergang von Lipid-Vesikeln: Effekt von $CrCl_3$ auf PC-Membranen. Universität Potsdam 2003.

Imparato, A.: Dynamic and Elastic properties of Fluid Bilayer Membranes. Universität Potsdam 2003.

Klumpp, S.: Movement of Molecular Motors: Diffusion and Directed Walks. Universität Potsdam 2003.

Valencia, A.: Condensation and Crystallization on Patterned Surfaces. Universität Potsdam 2003.

Bischofs, I.: Elastic Interactions of Cellular Force Patterns. Universität Potsdam 2004.

Illya, G.: Bilayer Material Properties and Domain Formation from Dissipative Particle Dynamics. Universität Potsdam 2004.

Nikolov, V.: Model membranes grafted with long polymers. Universität Potsdam 2004.

Uyaver, S.: Simulations of Annealed Polyelectrolytes in Poor Solvents. Universität Potsdam 2004.

Haluska, C. K.: Interactions of functionalized vesicles in the presence of europium (III) chloride. Universität Potsdam 2005.

Habilitations

Department of Colloid Chemistry:

Schlaad, H.: Polymer Self-Assembly: Adding Complexity to Mesostructures of Diblock Copolymers by Specific Interactions. Universität Potsdam 2004.

Department of Interfaces:

Kurth, D. G.: Self-Assembly of Hierarchically Structured Architectures of Metallo-supramolecular Modules. Universität Potsdam 2003.

Theory Department:

Schwarz, U. S.: Forces and Elasticity in Cell Adhesion. Universität Potsdam 2004.

Personalien
Appointments and Honors

2003

Ruf an eine Universität

Appointments

PD Dr. habil. Thomas Fischer — PD Dr. habil. Thomas Fischer, Group Leader in the Department of Interfaces, accepted a position as Associate Professor at the Florida State University in Tallahassee.

Dr. habil. Katharina Landfester — Group Leader in the Department of Colloid Chemistry, accepted a position as Full Professor (C4) in Organic Chemistry (Macromolecular Chemistry and Organic Materials) at the University Ulm.

Prof. Reinhard Lipowsky — Director of the Theory Department, refused a chair appointment at the LMU Munich.

Dr. Monika Schönhoff — Group Leader in the Department of Interfaces, accepted a position as Associate Professor (C3) in Physical Chemistry at the University Munster.

Ehrungen/Mitgliedschaften/Honorarprofessuren

Honors/Memberships/Honorary Professorships

Prof. Markus Antonietti — Director of the Department of Colloid Chemistry, obtained the Goldschmidt-Elhuyar-Award of the La real Sociedad Espanola de Quimica 2003.

Dr. Gerald Brezesinski — Group Leader at the Department of Interfaces, was appointed as Guest Professor at the Utsunomiya University in Japan.

Prof. Helmuth Möhwald — Director of the Department of Interfaces, became new President of the German Colloid Society.

2004

Ruf an eine Universität

Appointments

Dr. Charl Faul — Group Leader in the Department of Colloid Chemistry, accepted a Lectureship in Materials Chemistry at the School of Chemistry, University of Bristol

Dr. Ulrich Schwarz — Emmy Noether junior research group leader in the theory division, accepted an appointment as member of the Interdisciplinary Center for Scientific Computing (IWR) and junior research group leader at the newly established Center for Modelling and Simulation in the Biosciences (BIOMS) at Heidelberg University.

Dr. Gleb Sukhorukov — Group Leader in the Department of Interfaces, accepted a position of Chair in Biomaterials at the Queen Mary University of London.

Dr. Regine v. Klitzing — Group Leader in the Department of Interfaces, accepted a position as Associate Professor (C3) in Physical Chemistry at the University Kiel.

Ehrungen/Mitgliedschaften/Honorarprofessuren

Honors/Memberships/Honorary Professorships

Prof. Peter Fratzl — Director of the Department of Biomaterials, was appointed as Honorary Professor at the Humboldt University Berlin.

Dr. Dirk G. Kurth — Group Leader in the Department of Interfaces, was appointed as Co-Director of a Joint Laboratory at the National Institute of Materials Science in Tsukuba, Japan.

Prof. Helmuth Möhwald — Director of the Department of Interfaces, was elected as Corresponding Member of the Austrian Academy of Sciences.

Prof. Helmuth Möhwald — Director of the Department of Interfaces, was appointed as Guest Professor at the Fudan University in Shanghai.

Dr. Richard Weinkamer — Group Leader in the Department of Biomaterials, obtained the Publication Award 2005 of the German Academy of the Osteological and Rheumatological Sciences for: Weinkamer, R., Hartmann, M.A., Brechet, Y. and Fratzl, P.: A stochastic lattice model for bone remodeling and aging, Phys. Rev. Lett. 93, 228102 (2004).

Wissenschaftliche Veröffentlichungen und Patente
Publications and Patents

Biomaterials

Aichmayer, B., Fratzl, P., Saller, G., Puri, S.: Surface-directed spinodal decomposition on a macroscopic scale in a nitrogen and carbon alloyed steel. Phys. Rev. Lett. 91, 015701&/1-4 (2003).

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