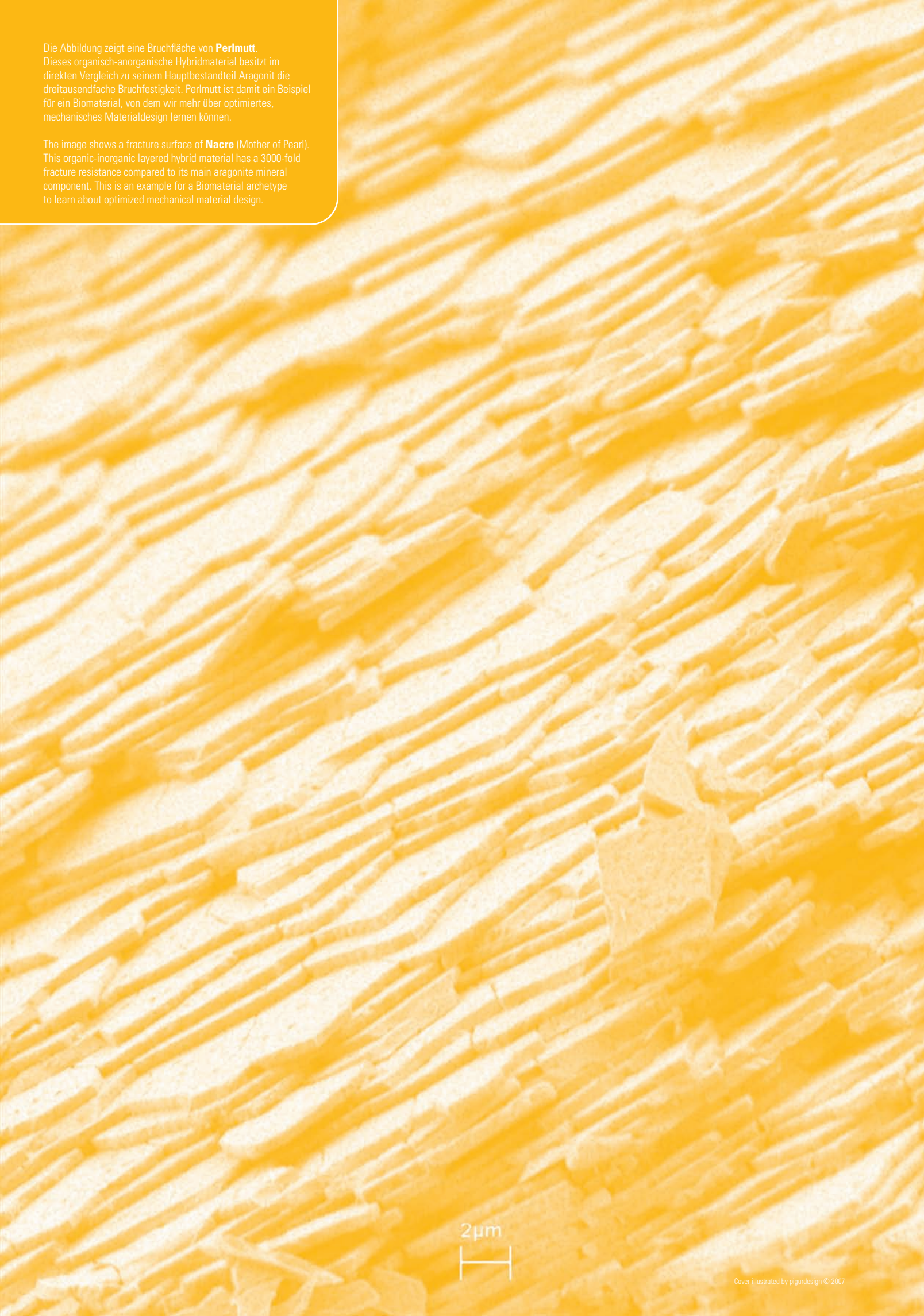
Max Planck Institute of Colloids and Interfaces

BIANNUAL REPORT 2005-2006

MAX-PLANCK-GESELLSCHAFT

Die Abbildung zeigt eine Bruchfläche von **Perlmutt**. Dieses organisch-anorganische Hybridmaterial besitzt im direkten Vergleich zu seinem Hauptbestandteil Aragonit die dreitausendfache Bruchfestigkeit. Perlmutt ist damit ein Beispiel für ein Biomaterial, von dem wir mehr über optimiertes, mechanisches Materialdesign lernen können.

The image shows a fracture surface of **Nacre** (Mother of Pearl). This organic-inorganic layered hybrid material has a 3000-fold fracture resistance compared to its main aragonite mineral component. This is an example for a Biomaterial archetype to learn about optimized mechanical material design.



Max Planck Institute of Colloids and Interfaces

BIANNUAL REPORT
2005-2006

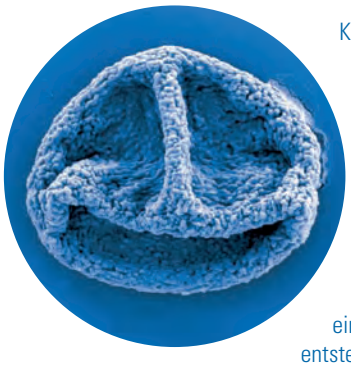
INHALTSVERZEICHNIS
TABLE OF CONTENTS

INTERFACES

THEORY & BIO-SYSTEMS

APPENDIX

Vorwort



Kolloide sind Teilchen oder Tröpfchen im Maßstab von weniger als einem Tausendstel Millimeter. Auch wenn man Teilchen dieser Größe ohne Mikroskop nicht sehen kann, sind sie doch allgegenwärtig. Praktisch alle natürlichen Gewebe in der belebten Natur sind aus Kolloiden aufgebaut. Sie finden sich auch in Farben, Cremes, Lebensmitteln, Medikamenten. Sehr viele dieser kleinen Objekte müssen zusammengefügt werden, bis ein sichtbarer und handhabbarer Gegenstand entsteht. Kolloidale Strukturen oder Materialien enthalten daher eine Vielzahl von Grenzflächen. Aus diesem Grund ist die Forschung an Kolloiden nicht von jener an Grenzflächen zu trennen. Da die typische Größe von Kolloiden im Bereich von Nanometern bis Mikrometern liegt, ist die Forschung an Kolloiden und Grenzflächen auch ein Teil der Nanowissenschaften.

Die Kolloid- und Grenzflächenforschung ist aber auch eine Wissenschaft, die in besonderem Maße von einer chemisch-physikalischen Betrachtung der Natur und einem biomimetischen Ansatz profitiert. Dabei werden Strukturen und Bauprinzipien, welche die Natur im Laufe der Evolution entwickelt hat, in künstliche Systeme und Materialien übertragen. Die Natur beherrscht es perfekt, aus nanometergroßen Bausteinen (Kolloiden) funktionelle Systeme wie Organe oder ganze Lebewesen zu assemblieren. Diese Möglichkeiten der Selbstaggregation spielen heute in der Chemie eine wesentliche Rolle und erlauben die direkte Synthese von komplexen, oft organisch-anorganischen Hybridsystemen mit interessanten physikalischen Eigenschaften. Auf diese Weise können Materialien hergestellt werden, die sich nicht nur selbst assemblieren, sondern sich auch an äußere Einflüsse anpassen oder nach einer Beschädigung heilen können. Die Eigenschaften solcher hierarchisch aufgebauter Materialien sind nur schwer zu untersuchen und noch schwerer vorherzusagen. Die Kolloid- und Grenzflächenforschung befasst sich daher auch mit der Physik von hierarchischen Materialien. Spezielle Messtechniken sind in diesem Bereich erforderlich, die es erlauben, Strukturen und – vor allem – Struktur-Funktions-Beziehungen über einen weiten Größenbereich von den kolloidalen Bausteinen bis zu makroskopischen Dimensionen zu erforschen. Schließlich ist Bewegung eine besondere Eigenschaft der belebten Natur, die in der Erforschung von aktiven Materialien oder molekularen Motoren ihre Entsprechung findet.

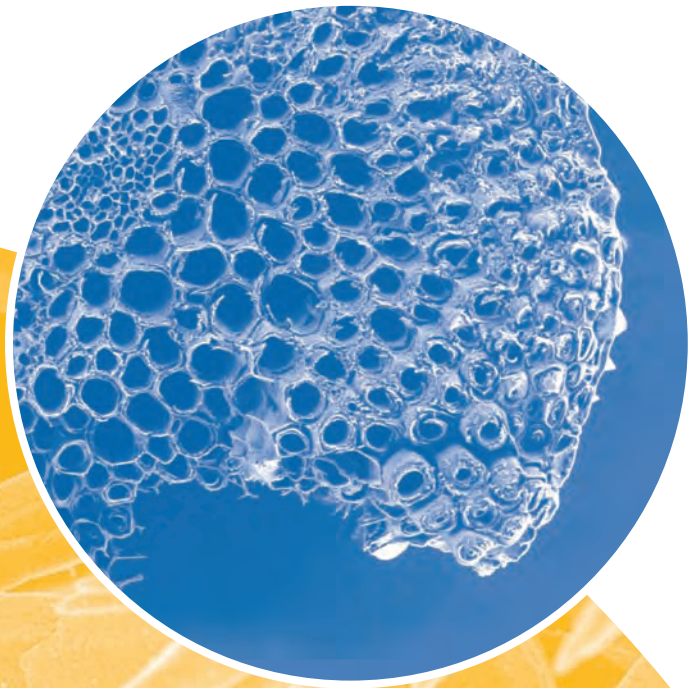
Folgerichtig hat sich die Forschung an biomimetischen Systemen zu einer zentralen Aktivität des Potsdamer Max-Planck-Instituts für Kolloid- und Grenzflächenforschug entwickelt. Das Institut besteht aus vier Abteilungen, die diese Thematiken aus verschiedenen Wissenschaftsdisziplinen heraus ansprechen. Die Forschung an Kolloiden und Grenzflächen umfasst die chemische Synthese and Analyse, die physikalische Beschreibung von Struktur, Eigenschaften und deren Beziehung, und die theoretische Modellbildung. Eine Verstärkung in Richtung biomolekularer Systeme wird diskutiert.

Auf Grund des interdisziplinären Forschungsgebietes ist der Personalstand des Instituts in mehrerer Hinsicht bunt. Zunächst betrifft das die wissenschaftliche Grundausbildung der Forschenden. Diese reicht von Chemie, Physik, Mathematik, Materialwissenschaft bis zur Biologie, Biochemie und sogar Medizin. Bunt ist auch die Herkunft der WissenschaftlerInnen, die je zu einem Drittel aus Deutschland, aus Europa und aus anderen Kontinenten stammen. Trotz dieser internationalen Ausrichtung ist das Institut sehr stark mit allen großen Universitäten in Potsdam und Berlin verbunden. Das drückt sich durch regelmäßige Lehrtätigkeit der Institutsmitarbeiter aus, aber auch durch eine Vielzahl von gemeinsamen Forschungsprojekten, zum Beispiel in Sonderforschungsbereichen oder EU-Netzwerken. Gemeinsam mit der Universität Potsdam und der Humboldt Universität zu Berlin betreibt das Institut die Internationale Max Planck Research School on Biomimetic Systems.

Die Forschungstätigkeit des Instituts ist grundlagenorientiert, aber dennoch anwendungsnah. Es gibt zusätzlich zu den Publikationen auch Anknüpfungspunkte und gemeinsame Projekte mit der Industrie, zum Beispiel in den Bereichen Chemie, Werkstoffe, Pharma oder Medizin. Dieses Buch enthält eine Vielzahl von Beispielen interessanter und wichtiger Forschungsergebnisse, berichtet jeweils auf zwei Seiten von den Forschern und Forscherinnen selbst. Mein herzlicher Dank gilt Ihnen und den Mitarbeitern und Mitarbeiterinnen in den technischen Bereichen und der Verwaltung, die gemeinsam diese Erfolge möglich gemacht haben.

In vielen der in diesem Buch besprochenen Forschungsthemen nimmt das Max-Planck-Institut eine bedeutende, oft sogar führende Stellung ein. Das wichtigste aber ist die Freude an der Forschung selbst. Erst diese Freude führt dazu, dass neue Themen mit Begeisterung aufgegriffen, Kooperationen quer über alle Fachgebiete konstruiert und echte Durchbrüche erzielt werden. Ich hoffe, dass Sie diese Begeisterung an manchen Stellen dieses Buches spüren und dass sich unsere Freude an der Kolloid- und Grenzflächenforschung auch auf Sie überträgt.

Peter Fratzl
Geschäftführender Direktor 2005-2006



Preface

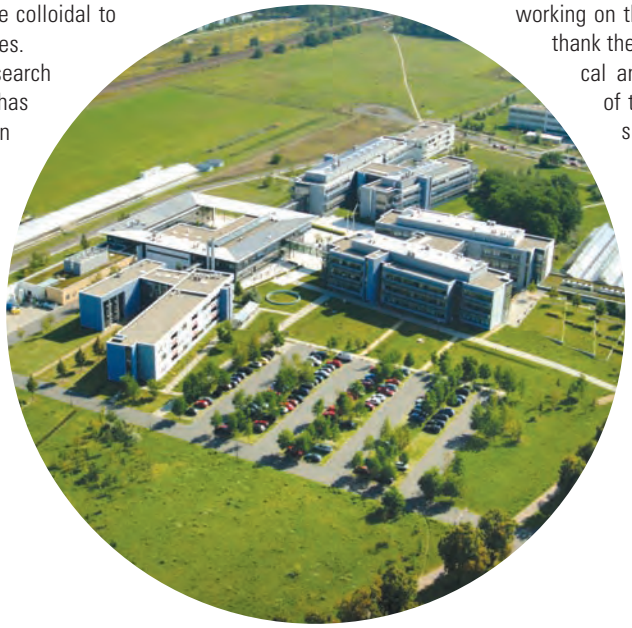
Colloids are particles or droplets in the size range below a thousandth of a millimetre. Particles of this size can not be seen without microscope, but they are omnipresent in the world around us. Practically all natural tissues in plants or animals are based on colloidal structures. Colloids are also found in paints, crémes, food or drugs. Many of these tiny particles have to be assembled to obtain a visible object. As a consequence, colloidal structures and materials contain a large amount of internal surface area between those particles. Therefore, research on colloids can not be separated from research on interfaces. Given the typical dimension of colloids in the range between nanometres and micrometres, colloid and interface science is also an important branch of the nanosciences.

Colloid- and interface science particularly profits from a biomimetic approach, where natural tissues are studied with the methods of chemistry and physics. Indeed, most functional natural systems, such as organs or whole organisms are assembled from nanometer sized building blocks. The goal of biomimetic research is to find out how nature has optimized biological structures during evolution and to use these principles to design new artificial biomimetic materials and systems. Self-assembly is one of these biomimetic principles and plays an important role in the chemical synthesis of complex molecular systems or hybrid materials with interesting physical properties. Using other approaches, the synthesis of materials with adaptive or even self-healing properties becomes conceivable. Controlled movement and motility are special properties of natural materials, and biomimetic research includes the study of active materials or molecular motors. Finally, complex materials with hierarchical structure require special methods of investigation which are able to characterise structure-function relations from the colloidal to the macroscopic size ranges.

As a consequence, research on biomimetic systems has become a central activity in the Max Planck Institute in Potsdam. The Institute has currently four Departments who address this topic as well as other subjects in colloids and interfaces from the viewpoint of different disciplines. Research covers chemical synthesis and analysis, physical description of structure, properties and their relationships, as well as theoretical modelling. A strengthening of the Institute in the direction of biomolecular systems is currently under discussion.

Due to the interdisciplinarity of the research fields, the scientists in the Institute have quite different scientific backgrounds. Their basic training reaches from Chemistry, Physics, Mathematics and Materials Sciences to Biology, Biochemistry and even Medicine. The origin of the scientists is also quite varied. About one third are from Germany, another third from Europe (excluding Germany) and the last third from the rest of the world, with a strong community from Asia, in particular China and India. Despite its international orientation, the Max Planck Institute of Colloids and Interfaces is closely tied to the major Universities in Potsdam and Berlin. This is expressed in particular by continued teaching activities by members of the MPI, but also by a number of joined scientific projects, for example in the framework of EU-Projects or collaborative research centres financed by the German Science Foundation (DFG). The International Max Planck Research School on Biomimetic Systems, a graduate program, is run together with Potsdam University and Humboldt University Berlin.

The Institute is devoted to basic research but the topics are often close to possible applications. Therefore, in addition to publications in peer-reviewed journals, there are also contacts to and joint projects with industry, for example with chemical, materials or pharmaceutical industry. This book contains many examples of exciting and important research results reported by the scientists working on these topics. I would like to thank them as well as all the technical and administrative members of the Institute who made this success possible in a continuous joint effort.



The
Max Planck
Institute of Colloids
and Interfaces holds an important
and sometimes leading position in some of the research topics covered by this book. The most important, however, is the pleasure associated with our scientific work. Only this enthusiasm makes it possible to pick up new exciting topics, build cooperations across disciplines and reach ground breaking results. I hope that you will feel this enthusiasm in reading the book and that we are able to convey to you some of our pleasure on working in colloid and interface science.

Peter Fratzl
Managing Director 2005-2006

Das Institut in Zahlen

I. Personal

Abb.1 zeigt deutlich, dass sich die Mitarbeiterzahl des Instituts einer Höchstgrenze von 270 genähert hat. Die Zahl wird einerseits durch den vorhandenen Platz beschränkt, der ca. 4000 m^2 beträgt und andererseits durch die Zahl der Planstellen. Die insgesamt vierzig angestellten Wissenschaftler können zudem nicht mehr als derzeit 150 Studenten und Postdocs ausbilden. Aber auch die siebzig Mitarbeiter in Verwaltung und Technik sind an der Grenze der personellen Auslastung.

Abb.2 demonstriert den stetigen Zuwachs an Doktoranden seit 2001. Das Jahr 2001 korrespondiert gleichzeitig mit einer sehr geringen Zahl an Diplomarbeiten in den Fächern Physik und Chemie in Deutschland. Der Anstieg der deutschen Studentenzahlen seitdem wird deutlich in der hier gezeigten Graphik. Die Zahl der ausländischen Studenten stieg ebenso aufgrund von speziellen europäischen Förderprogrammen.

Abb.3 Der Anteil der ausländischen Studenten und Postdocs am Institut beträgt konstant um 70%. Mehr als 50% der angestellten Wissenschaftler sind aus Westeuropa, 20% jeweils aus Osteuropa und China und 10% aus Indien. Diese Zahlen zeigen, dass das Institut sehr international ausgerichtet ist und viele junge Wissenschaftler aus der ganzen Welt ausbildet.

Etat

Der Gesamtetat hat sich mit der Erweiterung des Instituts durch die Abteilung Biomaterialien im Jahr 2003 weiter erhöht. Die Förderung durch Drittmittel betrug mit einigen Schwankungen in den letzten Jahren 2 Mio. EUR (siehe **Abb. 4**). Der hohe Anteil von DFG-Mitteln resultiert aus der Finanzierung von zwei Nachwuchsgruppen (Emmy Noether), die relativ hohe nichtöffentliche Förderung in den Jahren 2002/2003 aus den Preisgeldern für eine weitere Nachwuchsgruppe (Sofia Kovaleskaya). Darüber hinaus lassen sich folgende Trends feststellen (**Abb. 5**):

Abb.1

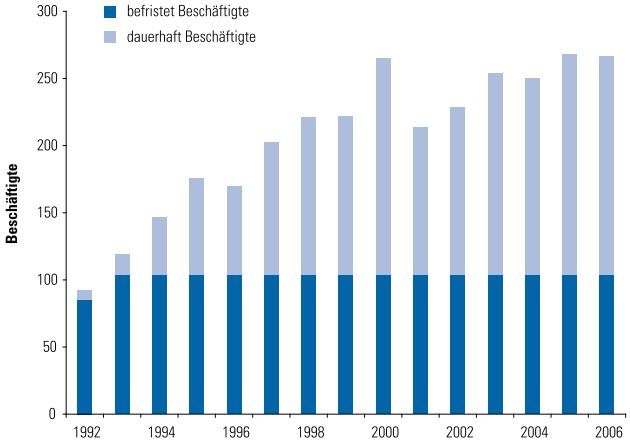


Abb.3

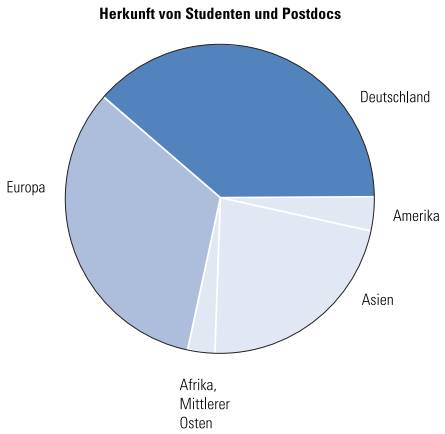
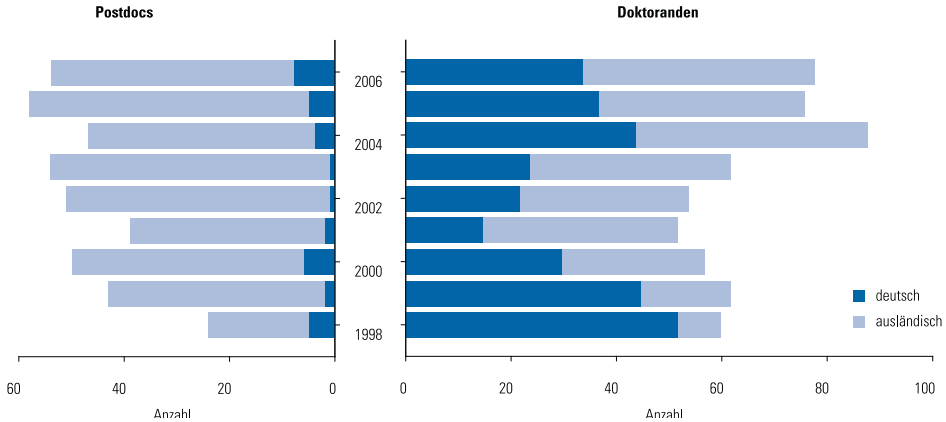


Abb.2



- Die direkte Förderung durch das Ministerium für Bildung und Forschung (BMBF) ist auf einen unerheblichen Betrag zusammengeschrumpft. Aufgrund neuer Richtlinien werden Max-Planck-Forscher jetzt von den regulären Programmen ausgeschlossen.

- Darüber hinaus werden viele Wissenschaftler auch aus dem DFG-Normalverfahren ausgenommen. Dies konnte durch stärkere Beteiligung an Schwerpunkten und Sonderforschungsbereichen kompensiert werden.

- Die Beschränkungen auf der nationalen Ebene werden größtenteils durch eine stärke Mitwirkung in EU-Programmen ausgeglichen. Diese Tendenz wird sich weiter fortsetzen.

- Die Industrieförderung beträgt ca. 15% der Drittmittel und entspricht der grundlagenorientierten Ausrichtung des Instituts.

Wissenschaftliche Ergebnisse und deren Einfluss

Die Qualität von wissenschaftlicher Arbeit lässt sich nur schwer messen. Dennoch zeigt **Abb. 6** als vorsichtige, quantitative Schätzung, dass die Anzahl von Publikationen in so genannten ISI Journals stetig auf jährlich 250-300 angestiegen ist. Die Zahl der Zitierungen hat mittlerweile sogar 9000 pro Jahr überschritten. Damit kann sich das Institut mit deutlich älteren und größeren Instituten messen. Der wissenschaftliche Einfluss wird auch in dem aktuellen Ranking der Humboldt-Stiftung deutlich. Ausgewertet werden die Entscheidungen ausländischer Spitzenwissenschaftler, die mit einem Stipendium oder einem Preis der Alexander von Humboldt-Stiftung ihren Arbeitsplatz an einer deutschen Forschungsinstitution frei wählen können. Darin belegt das Institut den zweiten Platz innerhalb der Max-Planck-Gesellschaft.

Abb.4

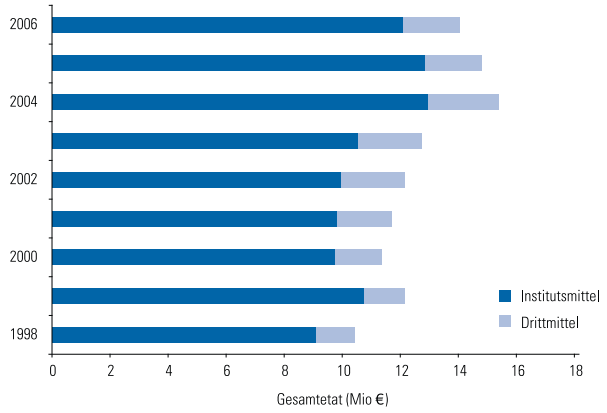


Abb.5

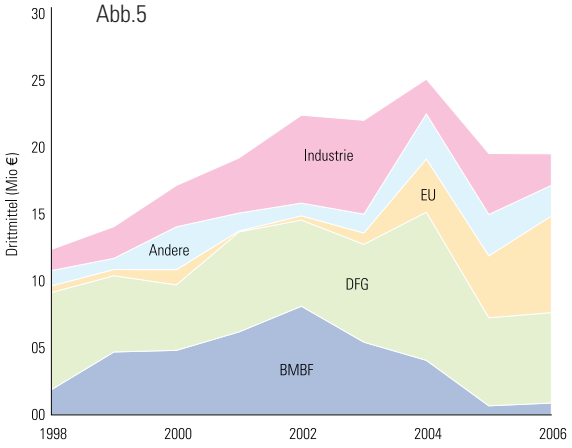


Abb.6 a

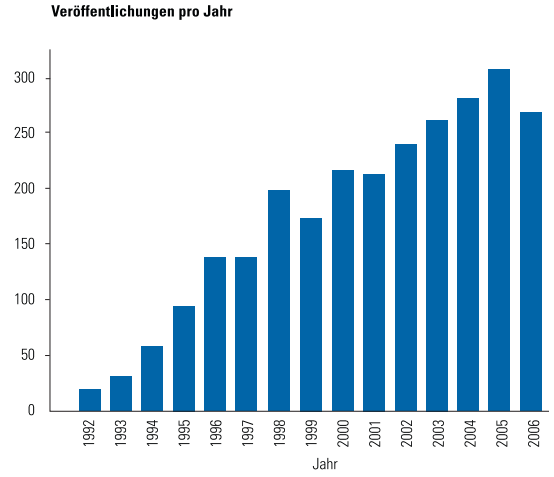
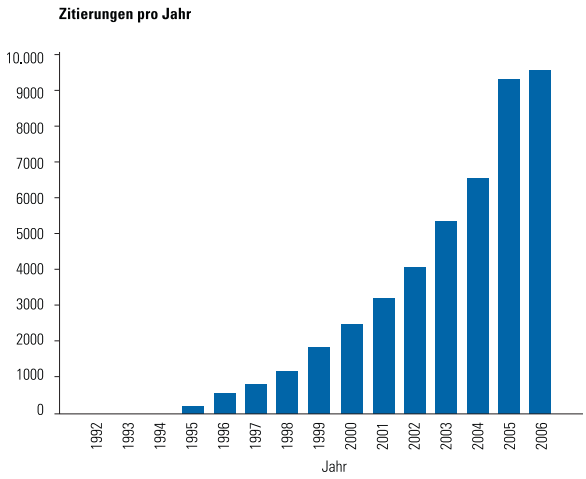


Abb.6 b



The Institute in Numbers

I. Personnel

Fig. 1 shows that the number of employees in the institute has reached a saturation near 270. This is on one hand limited by the space which amounts to about 4000m^2 on the other hand by the staff. The 40 staff scientists cannot train more than the present 150 students and postdocs, and also the 70 administrative and technical personnel are at the limits of capacity.

Fig. 2 demonstrates a steady increase of the number of PhD students since 2001. This year corresponded to a minimum number of diploma in physics and chemistry in Germany, and the recovery since then is reflected in the number of German students. The number of foreign students now increases due to specific European programmes.

Fig.3 The fraction of foreign students and postdocs is steadily around 70% but also more than 50% of the staff scientists are from Western Europe, 20% each from Eastern Europe and China, respectively, 10% from India. These numbers altogether show that the institute is truly international and that it trains many young scientists.

II. Budget

Whereas the overall budget has seen an increase since the extension by the Biomaterials department in 2003, the funding has remained steadily around 2 Mio Euro with some fluctuations between years and funding sources as sketched below (**Fig. 4**). The specially high total DFG funding in 2005 was due to the budgeting of two junior research groups (Emmy Noether) and the specially high non-public funding in 2002/2003 was due to a special award for a junior group (Sofia Kovaleskaya) counted then. Beyond these the special trends are the following: (**Fig. 5**)

Fig.1

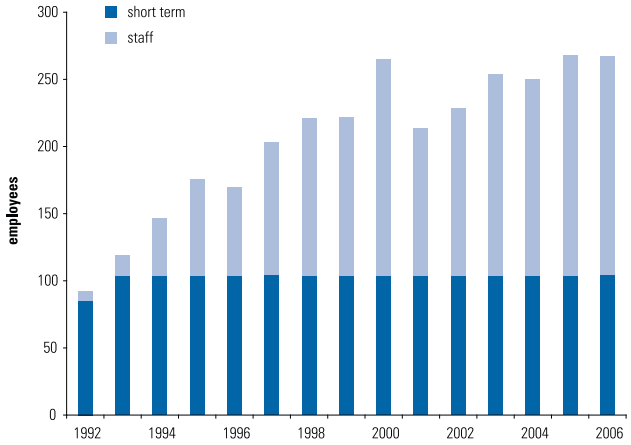


Fig.3

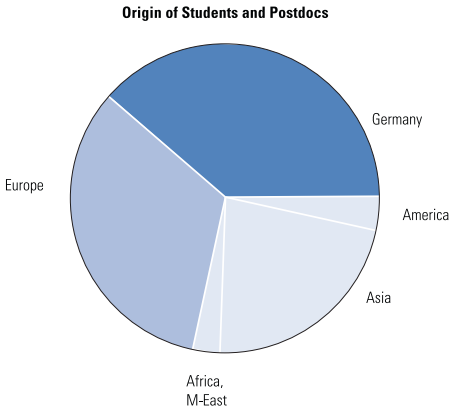
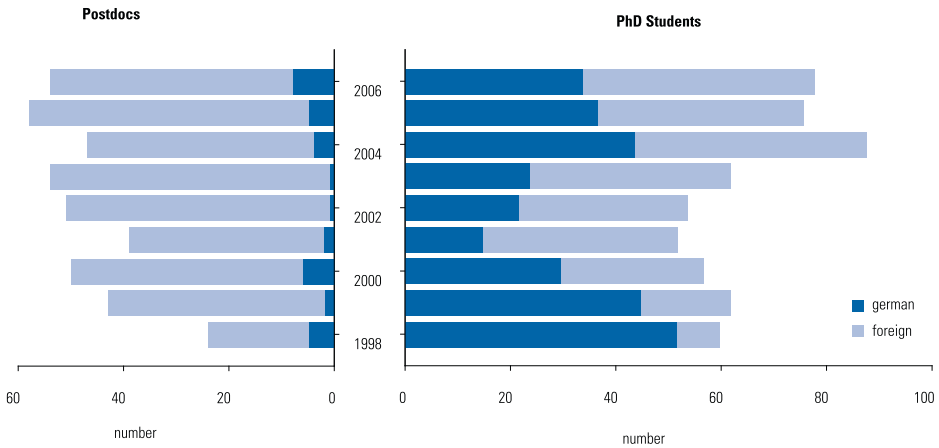


Fig.2



- The funding by the Ministry of Research and Technology (BMBF) has decayed to a nearly negligible amount. This has been politically enforced by new rules of the government excluding Max-Planck researchers from their regular programmes.

- Moreover, many of our researchers have been excluded from the regular DFG programmes. It could partly be compensated by stronger participation in priority programmes.

- The limitations on the national level could largely be overcome by a stronger involvement in EU-programmes, and this tendency will continue.

- The industry support amounts to around 15% of the funding. This is a accordance with the basic science mission of the institute.

III. Scientific Output and Impact

Obviously the quality of work is difficult to measure. As a quantitative estimate **Fig. 6** shows that the annual number of publications in ISI journals has steadily increased towards 250 - 300. The number of citations has meanwhile reached a level above 9000 per year which is comparable to values of much older and larger institutes. This increased impact is also reflected in the recent ranking of the Humboldt foundation, measuring the number of excellent young scientists having selected their host institute in Germany, where we are ranked second among all MPI's.

Fig.4

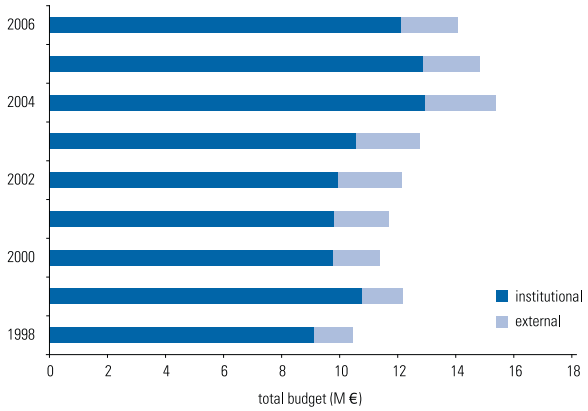


Fig.5

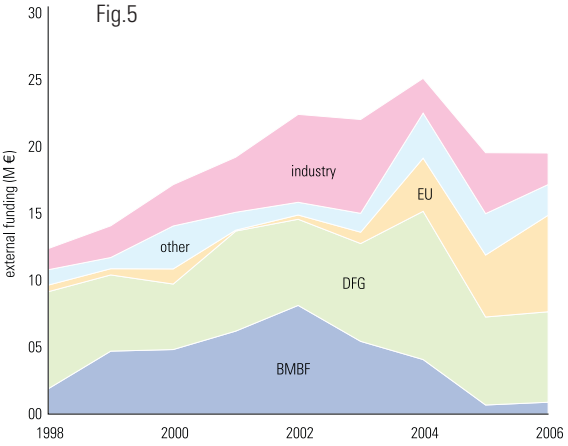


Fig.6 a

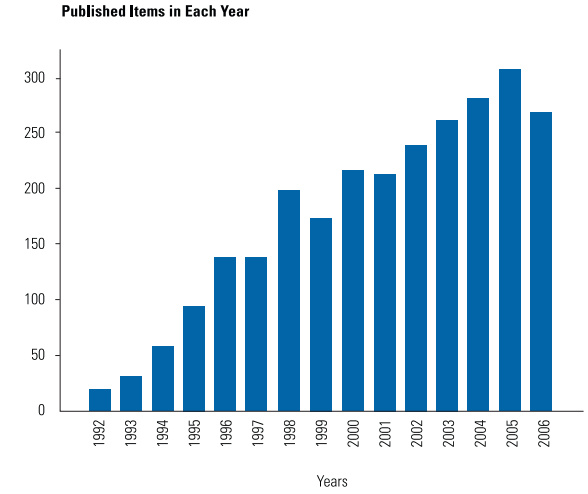
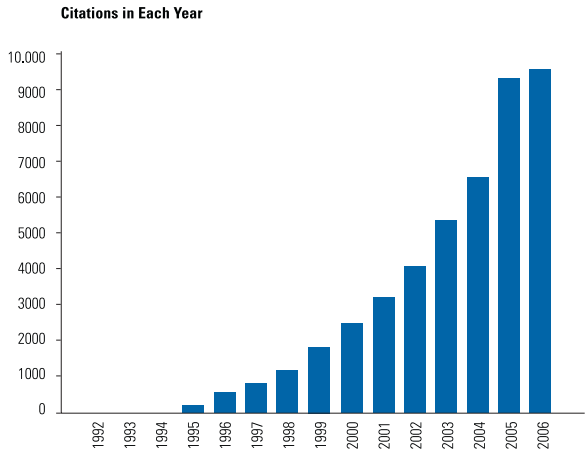


Fig.6 b



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

Die Kolloid- und Grenzflächenforschung befasst sich mit den Strukturen, die zwischen den Größenbereichen „Nano“ und „Mikro“ liegen und daher auch als Welt der versteckten Dimensionen bezeichnet werden. Darüber hinaus ist sie in der Lage, die Brücke zwischen Molekülen und biomimetischen Materialien oder biologischen Geweben zu schlagen. Wie in **Abbildung 1** zu sehen, sind zwei grundlegende Aspekte besonders bedeutend für die Forschung. Zum einen ermöglicht das Verständnis der strukturellen und dynamischen Hierarchien, kolloidale Strukturen mit größeren Einheiten zu verknüpfen. Zum anderen stellt die Aufklärung der generellen Mechanismen und Prinzipien, die auf biomimetische und biologische Systeme gleichermaßen angewendet werden können, einen einheitlichen, konzeptuellen Rahmen dar.

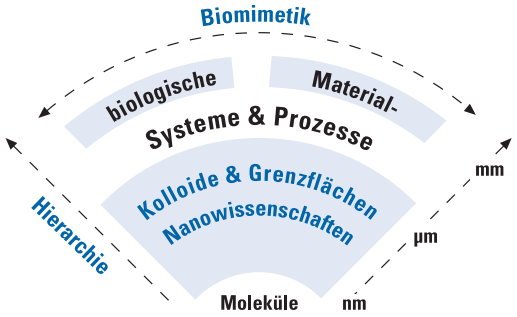


Abb. 1: Die Forschung am MPIKG beschäftigt sich mit Strukturen und Prozessen, die zwischen dem Nano- und Mikrometerbereich liegen, d.h. mit dem traditionellen Bereich der Kolloid- und Grenzflächenforschung, der viele Ebenen, angefangen von Molekülen bis hin zu biomimetischen Materialien und biologischen Geweben abdeckt.

Die Forschung am MPI für Kolloid- und Grenzflächenforschung basiert auf der Fachkenntnis von vier Abteilungen, die ein breites Spektrum an Methoden und Werkzeugen auf chemische Synthese, neue Materialien, physikalische Charakterisierung und theoretische Modellierung anwenden.

Die vielfältige Funktionsweise biomimetischer und biologischer Systeme hängt größtenteils von Struktur und Dynamik der Kolloide und Grenzflächen auf submikroskopischer Ebene ab. So können eine relativ kleine Menge von 20 Aminosäuren und vier Nukleotiden eine Vielzahl biologischer Polymere, Proteine und DNA mit nanometergroßen Strukturen ausbilden. Diese werden dann zu Filamenten, Membranen, Ribosomen und verschiedenen Biokolloiden zusammengebaut, die sogar Mineralien enthalten können. Diese Strukturen bilden die Grundlage der extrazellulären Matrix und der Zellen selbst und sind wesentlich 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 jeden Organismus'. In Analogie dazu hängen die Funktionalität von biomimetischen Materialien und deren mechanische, optische oder magnetische Eigenschaften in hohem Maße von den Strukturen ab, die auf der Nano- bis Mikrometerskala erzeugt werden.

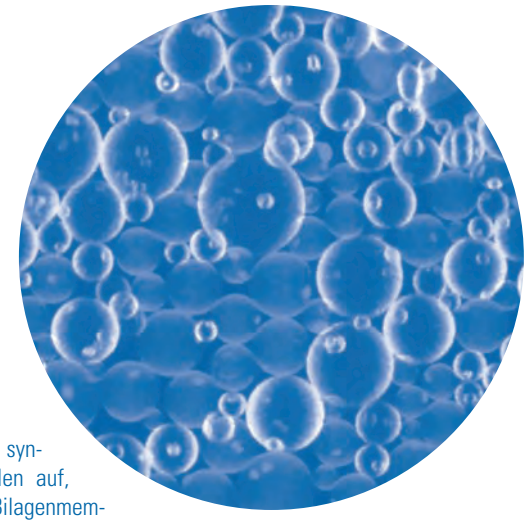
Kolloide und Grenzflächen

Die aktuelle Forschung am Institut konzentriert sich auf die Synthese, den Aufbau und die Analyse von natürlichen und künstlichen Mehrkomponenten-Systemen. 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.

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 die künftige Technologie und im Zuge des besseren Verständnisses biologischer Systeme auch die biomedizinischen Wissenschaften maßgeblich beeinflussen. So sind z.B. kolloidale Wirkstoff-Transportsysteme oder Veränderungen des Knochenmaterials aufgrund von Krankheit oder medizinischer Behandlung denkbar.

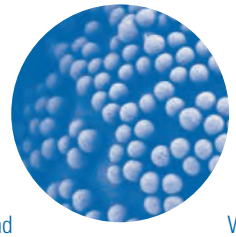
Die Synthese von funktionalen kristallinen oxidischen Nanopartikeln und neuen Kohlenstoffformen ist eine Spezialität des Instituts. Diese wird realisiert mit Hilfe von nichtwässrigen Sol-Gelrouten sowie hydrothermalen und bei hohen Temperaturen durchgeführten Karbonisierungen. Die dabei entstehenden 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.



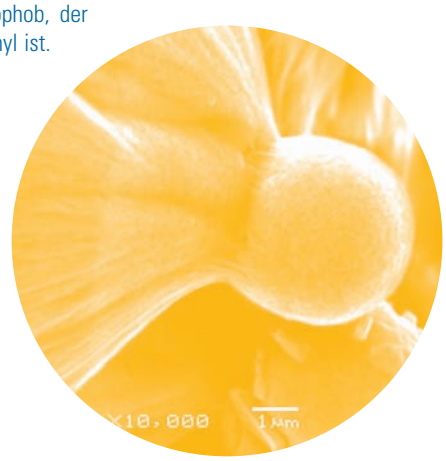
Für Wissenschaft und Anwendung ist neben weichen und harten Strukturen die kontrollierte Generierung von nanoskopischen Porengrößen für die Erzeugung von Bulk-Materialien und Filmen bedeutsam. Für die Bildung geeigneter Architekturen und Porengrößen in kristallinen Materialien werden daher Prozessvorlagen 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. Sie wurden zudem auch als Bausteine für supramolekulare Strukturen und Mikro- und Nanocontainer benutzt. Darüber hinaus konnten Methoden der supramolekularen Chemie erweitert werden, um funktionale Filme, reaktive Kapseln und sich selbst reparierende Beschichtungen zu erzeugen.



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. Andererseits können Polymere auch benutzt werden, um die Morphologie wachsender Partikel und Mineralien so zu verändern, dass organisch-anorganische Hybride entstehen.



Amphiphile Blockkopolymere weisen synthetische Analogien zu Lipidmolekülen auf, die in der Natur für die Bildung von Bilagenmembranen, Vesikeln und komplexeren räumlicheren Anordnungen verwendet werden. Vesikelmembranen können eine lineare Größe zwischen 30 Nanometern und 100 Mikrometern aufweisen. Als Konsequenz daraus variiert der Bereich von intramembranen Domänen über neun Größenordnungen zwischen kleinen Clustern von Lipidmolekülen und tausendstel Quadratmikrometern Membransegmenten.

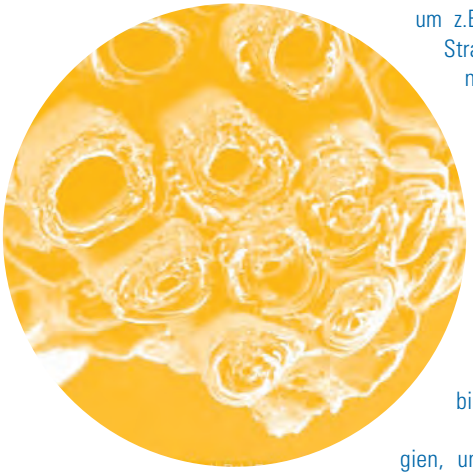
Die Anordnung von supramolekularen Strukturen wird von schwachen Wechselwirkungen (van der Waals Kräfte) oder entropisch induzierten Interaktionen (z.B. hydrophobischer Effekt) gesteuert. Die starke Abhängigkeit dieser Kräfte von umgebenden Parametern führt hin zu reaktiven und selbstheilenden Systemen.

Membranen und andere Grenzflächen können durch extra hinzugefügte Moleküle und Partikel funktionalisiert werden. Am MPIKG wurde eine überaus effektive Methode für die Bildung von eher komplexen Grenzflächenstrukturen entwickelt, die auf der nacheinander folgenden Ablagerung von negativ und positiv geladenen Polyelektrolyten basiert.

Darüber hinaus wird am Institut ein großes Spektrum an experimentellen Methoden genutzt, um Struktur und Dynamik von Kolloiden und Grenzflächen zu charakterisieren. Zudem werden verschiedene Methoden der chemischen Analyse verwendet. Eine entscheidende Herausforderung bildet die simultane Bestimmung von Mikro- und Nanometer großen 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 **Abb. 1**): aus der Analyse der Struktur- und Funktionsbeziehungen in den Zellen und der extrazellulären 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. Beispiele sind Homopolymere, die nur aus einem Typ von Monomer aufgebaut sind oder Doppelschicht-Membranen, die aus nur einer Lipidsorte 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, Vesikel, aus lipiden oder polymeren Doppelschichten 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 bei der theoretischen Beschreibung von biologischen und biomimetischen Systemen eingesetzt. Ersterer basiert auf der Thermodynamik von Grenzflächen und Membranen. Letzterer beginnt bei grob strukturierten Monomer-Modellen und deren Interaktionen, die mit einer Vielzahl von theoretischen Methoden aus der statistischen Physik 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 intermediate size range between "nano" and "micro" – some-times called the twilight zone or the world of hidden dimensions – and bridges the gap between molecules and biomimetic materials or biological tissues. As shown in **Fig. 1**, two aspects are particularly important in this type of research. The first is the understanding of structural and dynamical hierarchies in order to connect the nanoregime with much larger scales. The second aspect is the elucidation of basic mechanisms and general principles that apply both to biomimetic and to biological systems and, thus, provide a unified conceptual framework for both types of systems.

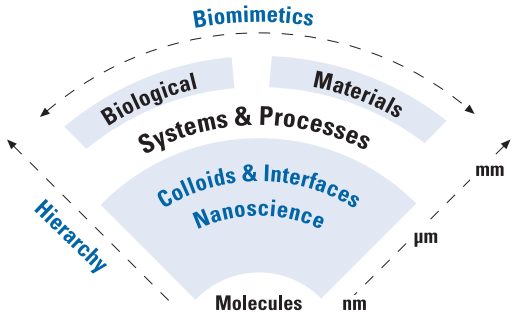


Fig. 1: Research in the MPIKG focuses on structures and processes in the size range between nano and micro, the traditional domain of colloid and interface science, covering many levels from molecules to biomimetic materials and biological tissues.

The versatile functionality of biomimetic and biological systems depends primarily on the structure and dynamics of colloids and interfaces in the nanoregime. 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 biocolloids which may contain mineral elements as well. These are the building blocks of the extracellular matrix and of the cells themselves, which form the basis of any living organism. This step from biopolymers to living cells covers the range from a few nanometers to many micrometers and is obviously crucial in constructing the complex architecture of organisms. In an analogous manner, the functionality of biomimetic materials and their 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 complex, multicomponent systems, both natural and artificial. 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.

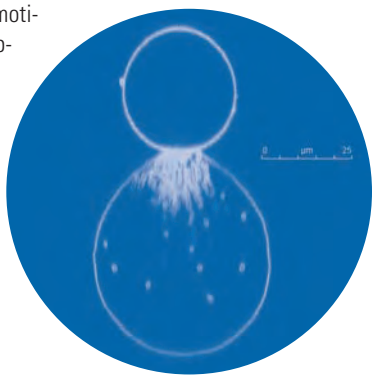
This interplay between experiment and theory is necessary in order to gain a deeper understanding of colloidal and interfacial systems. This understanding can then be used in order to improve the design of these systems, to optimize their performance, and to increase their reliability. In this sense, research at the MPIKG has a direct 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 the construction of drug-delivery systems based on colloidal structures or the small-scale characterization of changes in bone material arising from 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.

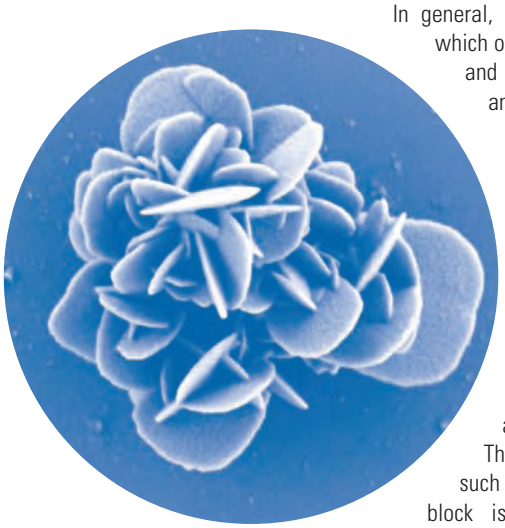
In addition to soft and hard structures, the controlled generation of nanoscopic pore channel systems into bulk materials and films is of great scientific and application interest. Here, template procedures are developed and applied to design the architecture and the size of pores in crystalline materials 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 concomitant 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. Methods of supramolecular chemistry have been extended to prepare functional films and responsive capsules as well as self-repairing coatings.

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 tissues: Bottom-up 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 at the MPIKG. For example, many methods of polymer synthesis are applied to create complex materials. These materials can be fully organic, such as block copolymers, for which one block is hydrophobic and the other is hydrophilic. Polymers can also be used to change the morphology of growing particles and minerals, leading to organic-inorganic hybrids.

Amphiphilic block co-polymers provide synthetic analogues of lipid molecules which are used by nature to form bilayer membranes, vesicles and more complex spatial compartments. Vesicle membranes can have a linear size between 30 nanometers and 100 micrometers. As a consequence, the area of intramembrane domains can vary over nine orders of magnitude between small clusters of a few lipid molecules and membrane segments of thousands of square micrometers. The assembly of supramolecular structures is governed by weak interactions such as van der Waals forces or entropically induced interactions such as the hydrophobic effect. The dependence of these forces on environmental parameters leads to responsive and self-healing systems.

Membranes and other interfaces can be functionalized by decorating them with additional molecules and particles. A powerful method to create rather complex 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 arrow in **Fig.1**: from the biological systems to the synthetic materials and vice versa. First, the analysis of structure-function relations in cells and extracellular matrix (from a physicochemical 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.

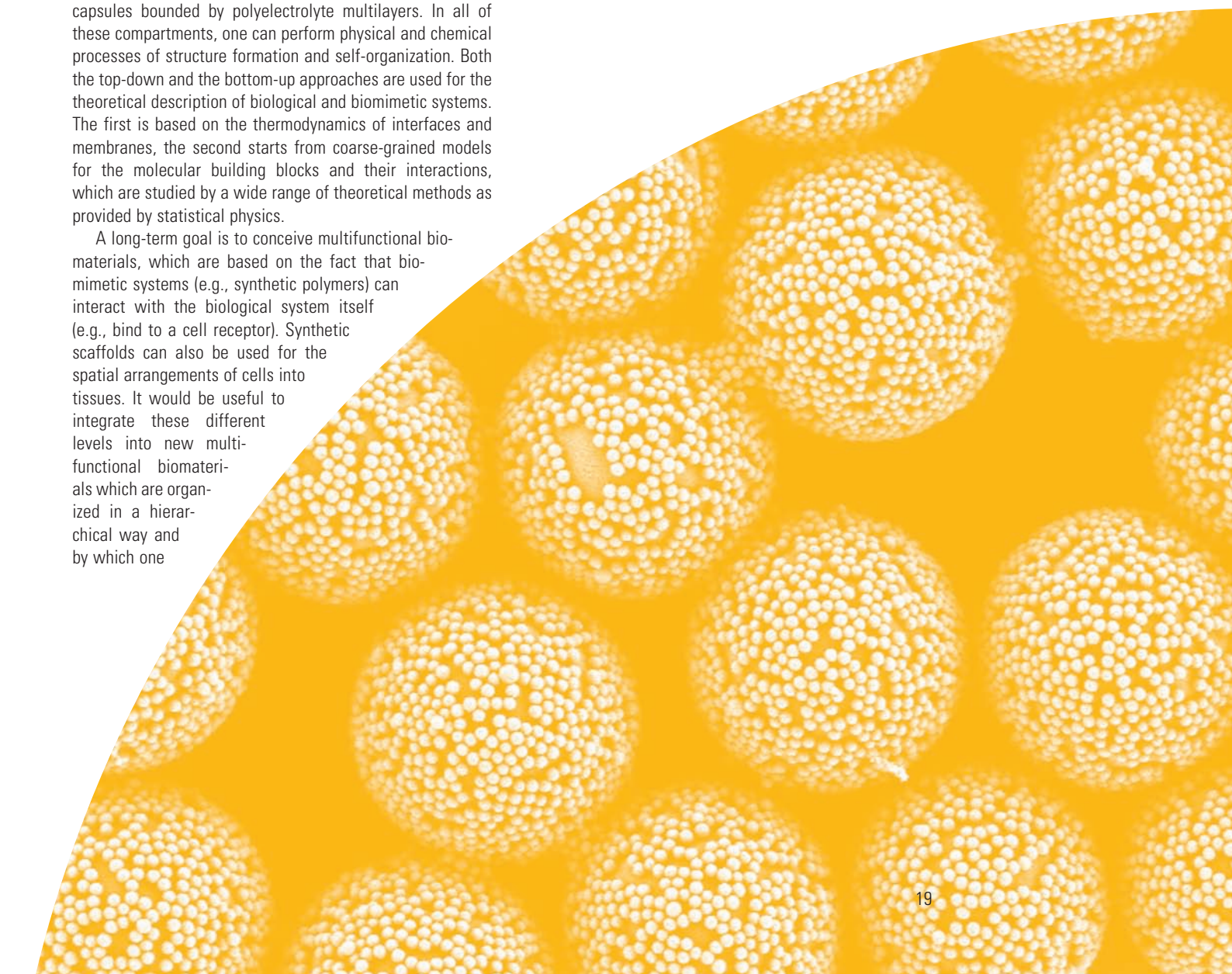
Research at the MPIKG involves the study of natural materials, such as plant cell walls, connective tissue and bone, their properties and their capability to heal and adapt to changing environmental conditions. Work on biomimetic systems includes the construction and study of different types of compartments: 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 molecular building blocks 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

Kooperationen mit Universitäten:
Zwischen dem Max-Planck-Institut für Kolloid- und Grenzflächenforschung (MPIKG) 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. Dies spiegelt sich in einer intensiven Lehrtätigkeit sowohl in Bereichen des Grundstudiums als auch in den Wahlpflichtfächern wider. Prof. Fratzl und Prof. Lipowsky sind Honorarprofessoren an der Humboldt Universität zu Berlin. Ein Kooperationsvertrag mit dieser Universität wurde bereits unterzeichnet. Darüber hinaus wurde Prof. Rabe vom Institut für Physik der Humboldt-Universität zu Berlin 2005 als Auswärtiges Wissenschaftliches Mitglied an das MPI für Kolloid- und Grenzflächenforschung berufen.

Die International Max Planck Research School über „Biomimetische Systeme" ist ein Graduierten-Kolleg, das zunächst gemeinsam mit der Universität Potsdam eingerichtet wurde und an der sich seit 2006 auch die Humboldt-Universität zu Berlin und die beiden Fraunhofer-Institute in Golm beteiligen. Sprecher der Schule ist Prof. Lipowsky, der die Schule 1999 beantragt hat.

Zur weiteren Verstärkung der Zusammenarbeit wurden zwei Juniorprofessuren an der Universität Potsdam eingerichtet: durch die Abteilung Kolloidchemie Prof. Andreas Taubert und durch die Abteilung Grenzflächen Prof. Matias Bargheer.

Das Institut ist über den Sonderforschungsbereich (SFB) 448 „Mesoskopische Verbundsysteme" sowie dem SFB „Muskel-Skelett-Regeneration", der von der Charité - Universitätsmedizin Berlin koordiniert wird, mit der Universität Potsdam und allen drei Berliner Universitäten verknüpft. Darüber hinaus ist es auch Mitglied des vom Bundesministerium für Bildung und Forschung (BMBF) finanzierten Berlin-Brandenburger Zentrums für Regenerative Therapien. Eine Plattform für die Untersuchung biologischer Proben mit Synchrotronstrahlung wird in enger Kooperation mit der Universität Heidelberg aufgebaut.

Internationale und Nationale 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 zehn EU Projekte innerhalb des 6. Rahmenprogramms und ein weiteres startet Oktober 2007. Das Marie Curie Netzwerk über „Biomimetic Systems" und das STREP-Netzwerk über „Active Biomimetic Systems" wird von der Theorieabteilung des MPI koordiniert. Weitere Informationen zu diesen beiden Netzwerken 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 Deutschen Forschungsgemeinschaft (DFG), der German Israel Foundation (GIF) for Scientific Research and Development, den National Institutes of Health (NIH) sowie der VW- und Zeit-Stiftung bestehen zur Zeit mit Australien, Bulgarien, Dänemark, Frankreich, der Gemeinschaft Unabhängiger Staaten (GUS), Italien, Israel, Schweiz, Ukraine und den USA. Darüber hinaus wird in enger Zusammenarbeit mit dem Ludwig-Boltzmann Institut für Osteologie in Wien (Österreich) an klinisch orientierter Knochenforschung gearbeitet.

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

Großes Engagement gilt auch 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.

Die Abteilung Grenzflächen unterhält 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). Die Abteilung Kolloidchemie hat 2001 zusammen mit dem Hefei National Laboratory for Physical Sciences at Microscale (CAS) eine Internationale Partnergruppe in Hefei eingerichtet.

Im Weiteren liefen in 2004 die aus dem strategischen Innovationsfonds der MPG geförderten Projekte „Plant Cell Wall" und „ENERCHEM (Nanochemische Konzepte einer nachhaltigen Energieversorgung)" sehr erfolgreich an. ENERCHEM ist ein Forschungsverbund von fünf Max-Planck-Instituten zur Entwicklung nanochemischer Lösungen für eine nachhaltige Energieversorgung. Das gemeinsam von den Max-Planck-Instituten für Kolloid- und Grenzflächenforschung, Festkörperforschung, Polymerforschung, Kohlenforschung und dem Fritz-Haber-Institut gegründete Projekt wird von Prof. Antonietti geleitet. Die Forschungsinitiative wird von der MPG mit insgesamt rund 4 Mio. Euro aus dem Strategischen Innovationsfonds gefördert.

Darüber hinaus kooperiert das Institut mit den Frauhofer-Instituten für Angewandte Polymerforschung und Biomedizinische Technologie und der Universität Potsdam in dem Projekt „Bioaktive Grenzflächen", in dem die Bindung von Biomolekülen und Zellen an funktionalisierte Oberflächen reversibel gesteuert werden soll. Der MPG-Anteil (aus dem

Strategiefonds) am Gesamtvolumen von 3.5 Mio. Euro beträgt 0.9 Mio. Euro.

Industriekooperationen, Verwertungsverträge, Ausgründungen

Industriekooperationen bestehen unter anderem mit der Clariant GmbH, Degussa AG, Procter & Gamble, Servier und der Schering AG. Das Institut hält gegenwärtig 46 Patente. Im Zeitraum von 1993-2000 erfolgten insgesamt sieben Ausgründungen: Capsulution Nanoscience AG, Colloid GmbH, Nanocraft GmbH, Optrel, Riegler & Kirstein, Sinterface und Oxidion GmbH.

Zusammen mit dem benachbarten Fraunhofer-Institut für Angewandte Polymerforschung wurde die Nachwuchsgruppe „Polymere Nanotechnologie für die Life Sciences" eingerichtet, in der neue Wege von Grundlagen hin zu Anwendungen beschritten werden sollen.

Perspektiven

In den letzten Jahren hat sich die Forschung an biomimetischen Systemen zunehmend als eine gemeinsame Klammer zwischen den Abteilungen entwickelt. Unterstützt wird die Verbreiterung des Themas durch die IMPRS „Biomimetic Systems" sowie durch die Mitwirkung in entsprechenden EU-Netzen. Das Institut sieht für seine langfristige Entwicklung das Erfordernis, auch das Thema „Biomolekulare Systeme" im Institut möglichst auf Abteilungsebene – ggf. in Kooperation mit einer Universität – abzudecken. Die Konzentration sollte dabei auf der Synthese und Manipulation biologischer Moleküle und künstlicher Nachbildungen und der Integration derselben in hierarchische Systeme liegen.

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. Des Weiteren informieren wir Sie über Mitgliedschaften in Fachbeiräten.

- Applied Rheology (M. Antonietti)
- Advances in Coll. Surf. Sci. (R. Miller, Herausgeber)
- Adv. Eng. Materials (P. Fratzl)
- Biophysical Reviews and Letters (P. Fratzl, R. Lipowsky, H. Möhwald)
- Calcif. Tissue Int. (P. Fratzl)
- Chemistry of Materials (M. Antonietti, H. Möhwald)
- Chem. Phys. Mat. (H. Möhwald)
- Colloids and Surfaces (J. Li, Herausgeber)
- Colloid & Polymer Science (M. Antonietti)
- Current Opinion Coll. Interf. Sci. (H. Möhwald)
- Europhysics Letters (R. Lipowsky)
- Journal of Biological Physics (R. Lipowsky)
- J. Struct. Biol. (P. Fratzl)
- Langmuir (M. Antonietti, H. Möhwald)
- Lecture Notes in Physics (R. Lipowsky)
- Macromolecular Journals of VCh (M. Antonietti)
- Nach.Chem.Lab.Tech. (M. Antonietti)
- Nano-Letters (H. Möhwald)
- New Journal of Chemistry (M. Antonietti)
- New Rheol. J. (M. Antonietti)
- PhysChemChemPhys (H. Möhwald)
- Polymer (M. Antonietti)
- Progress in Polymer Science (M. Antonietti)
- Review in Molecular Biotechnology (M. Antonietti)
- Soft Matter (H. Möhwald, Herausgeber)

Fachbeirat:

- Austrian Nano Initiative (H. Möhwald, Beirat und Jury)
- DECHEMA Arbeitsgruppe über „Chemische Nanotechnologie" (H. Möhwald)
- European Colloid and Interface Society (H. Möhwald, Präsident)
- Fraunhofer-Institut für Angewandte Polymerforschung (H. Möhwald)
- Gerhardt Schmidt Minerva Zentrum für supramolekulare Strukturen (P. Fratzl)
- German Colloid Society (H. Möhwald, Vorsitzender)
- Hahn-Meitner-Institut (H. Möhwald, Vorsitzender)
- Institut für Schichten und Grenzflächen, Forschungszentrum Jülich (H. Möhwald)
- Institute of Theoretical Physics, CAS (R. Lipowsky)
- Minerva Weizmann Komitee (R. Lipowsky)
- PETRA III Microfocus Beamline (P. Fratzl)
- Photon Science Committee DESY (P. Fratzl, Vorsitzender)

Scientific Relations

National Cooperations:
Cooperations with Universities
The Max Planck Institute of Colloids and Interfaces (MPIKG) and the University Potsdam maintain intense and well-connected research cooperations that are among others documented by a cooperation agreement from 1995. Prof. Antonietti, Prof. Lipowsky and Prof. Möhwald hold Honorary Professorships at the University Potsdam which reflect intensive teaching in basic studies as well as in specialized subjects. In addition to this Prof. Fratzl and Prof. Lipowsky hold Honorary Professorships at the Humboldt University Berlin. A cooperation agreement with the University and the MPIKG has already been signed. In 2005 Prof. Rabe of the Humboldt University Berlin (Institute of Physics) was appointed as Foreign Member of the Max Planck Institute of Colloids and Interfaces.

The "International Max Planck Research School on Biomimetic Systems" (IMPRS) is a graduate program, which was initiated together with the University of Potsdam and now involves the Humboldt University Berlin and the two Fraunhofer Institutes in Golm as well. The speaker of the school is Prof. Lipowsky who proposed the school in 1999.

For additional intensification of the collaboration two Junior Professorships were established at the University Potsdam: Prof. Matias Bargheer (Department of Interfaces) and Prof. Andreas Taubert (Department of Colloid Chemistry).

Besides this the institute is connected with the University Potsdam and with all three Berlin universities through the German Research Foundation (DFG) priority program "Mesoscopic Composites", as well as the new SFB program "Musculoskeletal Regenaration" coordinated by Charité, Medical University, Berlin. The MPI is also member of the BMBF-financed Berlin-Brandenburg Center for Regenerative Therapies (BCRT). Furthermore a platform for investigating biological specimens at Synchrotron BESSY is set up together with the University Heidelberg.

International and National Cooperations:
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 ten EU projects within the 6th framework program at the MPIKG. Another one will start in October 2007. The Marie Curie network on "Biomimetic Systems" and the STREP network on "Active Biomimetic Systems" are coordinated by the Theory & Bio-Systems Department of the MPI. Further information is available under www.biomimeticsystems.de and www.biomics.de.

Beyond the collaborations described there exist bilateral and cooperation projects under assistance of the European Space Agency (ESA), the German Academic Exchange Service (DAAD), the German Research Foundation (DFG), German Israel Foundation (GIF) for Scientific Research and Development, the National Institutes of Health (NIH), VW- and Zeit-Stiftung in Australia, Bulgaria, Commonwealth of Independent States (CIS), France, Italy, Israel, Denmark, Switzerland, Ukraine and USA. Clinically oriented bone research is carried out in close collaboration with the Ludwig Boltzmann Institute of Osteology in Vienna (Austria).

In addition the MPIKG has coordinated a German-French Collaborative Research Group which consists apart from the 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.

Also the maintainance and build-up of beamli-nes 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 cooperation agreements especially with BESSY and the Federal Institute for Materials Research and Testing for building-up and implementing a microfocus beamline.

Moreover the Department of Interfaces has established together with the Chinese Academy of Sciences an International Joint Laboratory in Beijing and a Joint Laboratory with the National Institute for Materials Science in Tsukuba (Japan). In addition the Department of Colloid Chemistry together with the Hefei National Laboratory for Physical Sciences at Microscale (CAS) started an International Partner Group in Hefei in 2001.

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. EnerChem is a research association, initiated by five Max Planck institutes and coordinated by Prof. Antonietti of the MPIKG. The aim is to combine the chemical expertise and capacities of these institutes to generate solutions to the emerging problems of energy supply, storage and saving with the focus on nanostructured carbon materials. The research initiative is funded with 4. Mill. EUR.

Furthermore a cooperation project between the institute and the Fraunhofer Institutes of Applied Polymer Research and Biomedical Technology and the University Potsdam called "Bioactive Interfaces" has been established. The research project is funded with altogether 3.5 Mill EUR. The part of the strategic innovation funds of the Max Planck Society amounts 0.9 Mill EUR.

Cooperations with Industry, Application Contracts, Spin-Offs

Among many industry contacts cooperations with well-defined targets have been with Clariant GmbH, Degussa AG, Procter & Gamble, Servier and Schering AG. At present the MPIKG upholds 46 patents. In the period from 1993-2006 seven spin-offs have been launched: Capsulution Nanoscience AG, Colloid GmbH, Nanocraft GmbH, Optrel, Riegler & Kirstein, Sinterface and Oxidion GmbH. Moreover a Junior Research Group "Nanotechnology for Life Science" has been established together with the neighbouring Fraunhofer Institute for Applied Polymer Research. This group should break new ground from basic research to application.

Perspectives

In the last few years research on biomimetic systems has increasingly developed as a common scientific subject matter of the four departments. This is supported by the IMPRS "on Biomimetic Systems" and the participation in the corresponding EU-networks. For the long-term development of the institute it is therefore necessary and essential to cover also the field of "Biomolecular Systems" and this preferably with a fifth department and in cooperation with an university. The concentration lies on the synthesis and manipulation of biological molecules and artificial simulations and on their integration into hierarchical systems.

Editorial and Advisory Boards

Scientists serve as reviewers and advisors for many journals. Therefore listed are only activities as editor and member of an editorial board. Moreover you will find a list where you can find memberships in advisory boards.

Editorial Boards

- Applied Rheology (M. Antonietti)
- Advances in Coll. Surf. Sci. (R. Miller, Editor)
- Adv. Eng. Materials (P. Fratzl)
- Biophysical Reviews and Letters (P. Fratzl, R. Lipowsky, H. Möhwald)
- Calcif. Tissue Int. (P. Fratzl)
- Chemistry of Materials (M. Antonietti, H. Möhwald)
- Chem. Phys. Mat. (H. Möhwald)
- Colloids and Surfaces (J. Li, Editor)
- Colloid & Polymer Science (M. Antonietti)
- Current Opinion Coll. Interf. Sci. (J. Li)
- Europhysics Letters (R. Lipowsky)
- Journal of Biological Physics (R. Lipowsky)
- J. Struct. Biol. (P. Fratzl)
- Langmuir (M. Antonietti, H. Möhwald)
- Lecture Notes in Physics (R. Lipowsky)
- Macromolecular Journals of VCh (M. Antonietti)
- Nach.Chem.Lab.Tech. (M. Antonietti)
- Nano-Letters (H. Möhwald)
- New Journal of Chemistry (M. Antonietti)
- New Rheol. J. (M. Antonietti)
- PhysChemChemPhys (H. Möhwald)
- Polymer (M. Antonietti)
- Progress in Polymer Science (M. Antonietti)
- Review in Molecular Biotechnology (M. Antonietti)
- Soft Matter (H. Möhwald, Editor)

Advisory Boards:

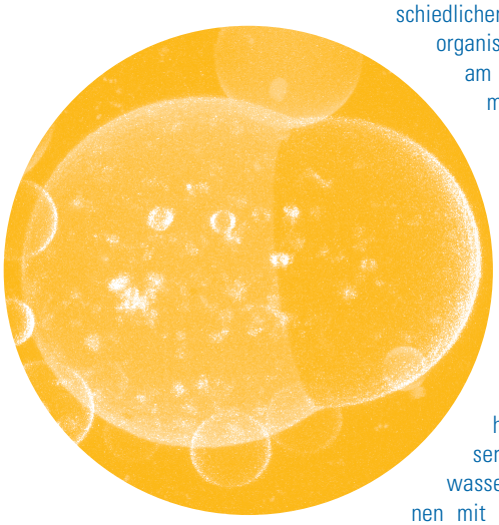
- Austrian Nano Initiative (H. Möhwald, Advisory Board and Jury)
- Bayrische Elitenetzwerke (R. Lipowsky)
- DECHEMA Research Group on "ChemicalNanotechnology" (H. Möhwald)
- European Colloid and Interface Society (H. Möhwald, President)
- Fraunhofer Institute for Applied Polymer Research (H. Möhwald)
- Gerhardt Schmidt Minerva Center on Supramolecular Architectures (P. Fratzl)
- German Colloid Society (H. Möhwald, President)
- Hahn-Meitner Institute (H. Möhwald, (Chair)
- Institute of Thin Films and Interfaces
- Research Centre Jülich (H. Möhwald)
- Institute of Theoretical Physics, CAS (R. Lipowsky)
- Minerva Weizmann Komitee (R. Lipowsky)
- PETRA III Microfocus Beamline (P. Fratzl)
- Photon Science Committee DESY (P. Fratzl, Chair)

Internationale Max Planck Research School (IMPRS) über Biommetische Systeme

Graduiertenprogramme über Biomimetische Systeme
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 seit 2004 das European Early Stage Training (EST), das aus einem Netzwerk von sechs europäischen Gruppen in Kopenhagen, Düsseldorf, Edinburgh, Leoben, Mailand und Toulouse besteht.

Zusammen mit seinen Partnern bietet das Institut ausländischen und deutschen Studenten der Physik, Chemie, Biologie und Materialwissenschaften ein interdisziplinäres Lehr- und Forschungsprogramm über „Biomimetische Systeme" an. Hauptziel des Graduiertenprogramms ist es, Grundlegende Kenntnisse über biologische und biomimetische Systeme zu vermitteln und damit eine fachübergreifende Ausbildung anzubieten. Die auf Englisch gehaltenen Kurse, Seminare und Workshops werden von international renommierten Dozenten des jeweiligen Forschungsgebietes gehalten.

1. Was sind biomimetische Systeme?
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 Membranen mit mehreren Lipidkomponenten; Diblock-Copolymerschichten und Polyelektrolyt-Multischichten; Membranfusion, aktiver Transport von molekularen Motoren; Biomineralisation und Knochen, Netzwerkdynamik und Evolution.

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) über „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 2007 eine Popularität erlangt, die bis in die Werbung und den Film reicht. Aufgrund dieser rasanten Entwicklung zeigt Google bei Sucheingabe heute mehr als eine Million Ergebnisse für „biomimetisch" und 800.000 für „biomimetische Systeme" an. Dabei steht unser EU Netzwerk EST beim Suchbegriff „Biomimetische Systeme" an zweiter und die IMPRS an vierter Stelle.

2. Lehrprogramme über Biomimetische Systeme
Das Max-Planck-Institut für Kolloid- und Grenzflächenforschung hat die große Bedeutung biomimetischer Systeme schon seit langem erkannt. Die Auseinandersetzung mit dieser Thematik erfolgte lange bevor diese als Trendbegriff in die Medien und die wissenschaftliche Gemeinschaft eingegangen ist. Die typische, traditionell ausgerichtete Ausbildung, die die meisten Studenten erhalten, reicht allerdings für ein befriedigendes Grundwissen in der Biomimetik nicht aus. Es gibt daher einen starken Bedarf an multidisziplinär geschulten Studenten, um diesen wachsenden Bereich ausreichend entwickeln und ausbauen zu können.

Der Antrag für die Internationale Max Planck Research School (IMPRS) on „Biomimetic Systems" wurde 1999 von einem von uns (R.L.) eingereicht und von der Leitung der Max-Planck-Gesellschaft bewilligt. Die Schule eröffnete daraufhin das erste Semester im Jahr 2000 und hat eine weitere Förderung bis 2012 erhalten. Darüber hinaus haben sich die andauernden Bemühungen, die Ausbildungsaktivitäten zu erweitern und zu verstärken 2003 in der Beantragung und 2004 mit der Koordination des Early Stage Training Network (EST) fortgesetzt. Das EST Netzwerk besteht aus sieben europäischen Partnern und wird von der Europäischen Gemeinschaft finanziert.

2.1 Die IMPRS über „Biomimetische Systeme"
Der Antrag für die Internationale Max Planck Research School (IMPRS) über „Biomimetische Systeme" wurde zunächst für einen Zeitraum von sechs Jahren (2000-2006) bewilligt. Nach erfolgreicher Evaluierung im Jahr 2004 wurde das Vorhaben, die Schule fortzuführen, durch die Leitung der Max-Planck-Gesellschaft bestätigt. Es wurde eine weitere Förderung von sechs Jahren bis zum Ende des Jahres 2012 festgesetzt.

Partner der Schule
Von 2000 bis 2003 bestand die IMPRS aus sieben Partnergruppen: den drei Abteilungen des MPI für Kolloid- und Grenzflächenforschung und vier Gruppen der Universität Potsdam. Die neu etablierte vierte Abteilung für „Biomaterialien" des MPIKG nahm 2003 ihre Arbeit auf und beteiligt sich seitdem ebenfalls an der Schule. Die Struktur der IMPRS bestand in dieser Weise bis zur Mitte des Jahres 2006.

Mit dem zweiten Bewilligungszeitraum (ab Mitte 2006) kamen weitere Gruppen hinzu: zwei Gruppen der Universität Potsdam, drei Gruppen der Humboldt-Universität zu Berlin, zwei Gruppen des Fraunhofer-Instituts für Biomedizinische Technik (IBMT) und eine Gruppe des Fraunhofer-Instituts für Angewandte Polymerforschung (IAP). Das Fraunhofer-Institut für Biomedizinische Technik ist im Sommer 2006 in den Wissenschaftspark Golm gezogen. Die Gruppen der Humboldt-Universität zu Berlin befinden sich in Berlin-Adlershof.

Weiterführende Informationen über die IMPRS on „Biomimetic Systems" und über die damit verbundenen Lehrveranstaltungen erhalten Sie unter www.imprs.org

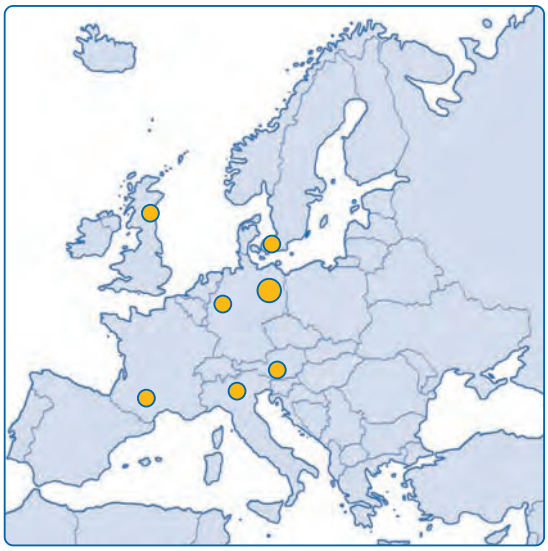


Abb.: Europakarte mit Partnern des EST Netzwerks (gelbe Kreise)

2.2 European Early Stage Training Network

Der Antrag für das Early Stage Training (EST) über „Biomimetische Systeme" wurde 2003 von uns (R.L. und A.V.) eingereicht und von der Europäischen Kommission für einen Zeitraum von vier Jahren (2004-2008) bestätigt. Die Förderung war stark umkämpft. So wurden im Bereich Physik nur fünf von mehr als 100 Anträgen akzeptiert. Die ersten EST-Studenten nahmen im September 2004 ihre Arbeit auf.

Partner des Netzwerks

Das EST-Netzwerk besteht im Wesentlichen aus den Gruppen der IMPRS (drei Abteilungen des MPIKG, zwei Gruppen der Universität Potsdam) sowie aus zusätzlichen Arbeitsgruppen des Niels-Bohr-Institutes in Kopenhagen, der Universität Düsseldorf, der Universität Edinburgh, der Technischen Universität in Leoben, dem Politecnico Mailand sowie der Universität Paul Sabatier in Toulouse (siehe Abbildung).

Weiterführende Informationen über das Marie-Curie Early Stage Training Netzwerk „Biomimetische Systeme" erhalten Sie unter http://www.biomimeticsystems.org.

2.3 Bio-Systeme EST Konferenz, Berlin 2006

Im Rahmen des Marie Curie EST über Biomimetische Systeme hat das MPI für Kolloid- und Grenzflächenforschung im Juni 2006 eine große Konferenz über Bio-Systeme organisiert. Innerhalb dieser Veranstaltung kamen 36 Sprecher des EST-Netzwerks und andere namhafte Persönlichkeiten auf dem Gebiet der biologischen und biomimetischen Systeme aus ganz Europa und den USA zusammen. Weiterführende Informationen erhalten Sie unter: http://www.bio-systems.org/berlin2006

2.4 Bio-Systeme Sommerschule, Peking 2006

Das Institut ist sehr daran interessiert, die bereits bestehenden Verbindungen zu nationalen und internationalen Partnern aufrechtzuerhalten und zu stärken sowie neue Kooperationen aufzubauen. Besonderes Interesse gilt dabei Regionen, in denen Wissenschaft und Forschung besonders gefördert werden. Aus diesem Grund hat das MPIKG großes Interesse an Veranstaltungen in China.

Im September/Oktober 2006 wurde daher eine zweiwöchige Sommerschule über Bio-Systeme zusammen mit unseren Partnern der Chinesischen Akademie der Wissenschaften (CAS) organisiert. Mit Vortragenden aus Europa, den USA und China bot diese Veranstaltung den rund 60 Masterstudenten und Doktoranden einen grundlegenden, multidisziplinären Überblick über biologische und biomimetische Systeme. Weiterführende Informationen erhalten Sie unter: www.bio-systems.org/beijing2006

3. Ausblick

In den nächsten zwei Jahren werden einige der genannten Projekte abgeschlossen sein und wiederum neue Projekte, Konferenzen und Sommerschulen realisiert werden. Das Graduiertenprogramm ist Teil einer größeren Reihe von Aktivitäten, die sich mit dem aktuellen und vielfältigen Forschungsthema „Bio-Systeme" befassen.

Gesammelte Informationen dazu finden Sie unter www.bio-systems.org.

Reinhard Lipowsky
und Angelo Valleriani

International Max Planck Research School (IMPRS) on Biomimetic Systems

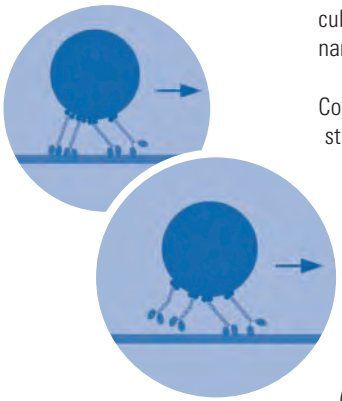
Graduate Programs on Biomimetic Systems

The MPI of Colloids and Interfaces is involved in two graduate programs on "Biomimetic Systems". First, in the year 2000 it has established, together with the University of Potsdam, an International Max Planck Research School (IMPRS) on this topic. Second, since the year 2004 the MPI also coordinates a European Early Stage Training (EST) network which includes six partner groups in Copenhagen, Düsseldorf, Edinburgh, Leoben, Milano, and Toulouse.

Together with its partner groups the MPI of Colloids and Interfaces offers an 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 in biological and biomimetic systems, which transcend the traditional boundaries between the different disciplines. The curriculum is based on courses, seminars and workshops that are offered by scientists active in this field.

1. What are Biomimetic Systems?

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; biomineralization and bone; networks dynamics and evolution.

At present, biomimetic systems are a hot research topic around the world. In the year 1999, when our International Max Planck Research School (IMPRS) 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 end of 2006, "biomimetic" has become a popular term that is mentioned even in movies and advertisements, and Google returns more than 1 million results for it and it returns about 800000 results for "biomimetic systems"! In fact, our EU-Network EST is currently returned as the second result for "biomimetic systems" and our IMPRS as the fourth one.

2. Training Programs on Biomimetic Systems

The Max Planck Institute of Colloids and Interfaces recognized the relevance of Biomimetic Systems long before the word had so much resonance in the media and in the scientific community as it has now. We also realized that the typical traditional training of most students would not provide a sufficient knowledge base in biomimetics. Thus, there is a strong demand of multidisciplinary training in order to further develop this research area which has many possible applications in bioengineering, pharmacology and medicine.

Thus, already in the year 1999 one of us (R.L.) submitted a proposal for the International Max Planck Research School on Biomimetic Systems (IMPRS) to the President of the Max Planck Society. This proposal was approved and the school started with its first semester in the year 2000 and will run until 2012. On the other hand, in the continuous effort to enlarge and strengthening our training activity in 2003 we have established a seven-partner Early Stage Training Network (EST) financed by the European Commission in 2004.

2.1 The IMPRS on Biomimetic Systems

The school was originally approved for the duration of six years until mid 2006. After a successful evaluation in 2004, our proposal for continuation was approved by the President of the Max Planck Society and now the school will run for another six years until the end of 2012.

Partners of the School

From 2000 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. This structure of the school persisted until mid 2006.

Starting with the second period, from mid 2006, several groups joined the school: Two additional groups from the University of Potsdam; three groups from Humboldt University Berlin; two groups from the Fraunhofer Institute for Biomedical Engineering (IBMT) and one group from the Fraunhofer Institute for Applied Polymer Research (IAP).

The Fraunhofer Institute for Biomedical Engineering moved to the Science Park in Potsdam-Golm during the summer 2006. The groups from Humboldt University are located in Adlershof, Berlin.

More detailed information about the International Max Planck Research School on "Biomimetic Systems" can be found on its website at http://www.imprs.org.

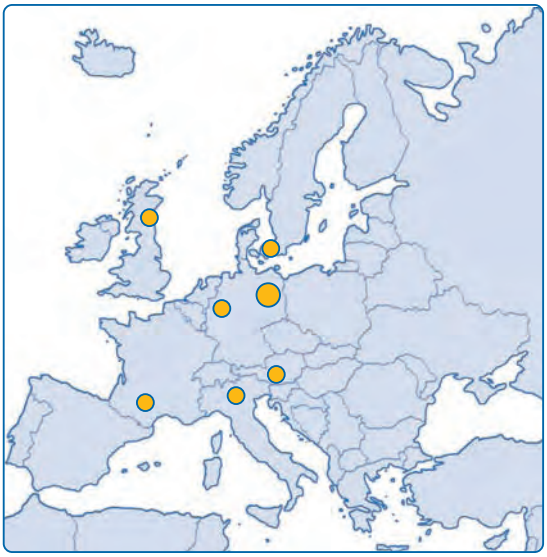


Fig.: A map of Europe with the partners of the EST network indicated by yellow dots.

2.2 European Early Stage Training Network

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

Partners of the Network

The EST network consists of most groups from IMPRS (three departments of the MPI, two 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 Politecnico of Milano, and The University Paul Sabatier of Toulouse, see Figure.

More detailed information on the Marie-Curie Early Stage Training Network on "Biomimetic Systems" can be found on its website at http://www.biomimeticsystems.org.

2.3 Bio-Systems EST Conference, Berlin 2006

Within the framework of our Marie Curie EST on Biomimetic Systems, the MPI has organized a big conference on Bio-Systems in June 2006. This conference has brought together 36 speakers from the EST network, the rest of Europe and the US, who covered many timely and exciting aspects of biological and biomimetic systems. For more information, see:
http://www.bio-systems.org/berlin2006

2.4 Bio-Systems Summer School, Beijing 2006

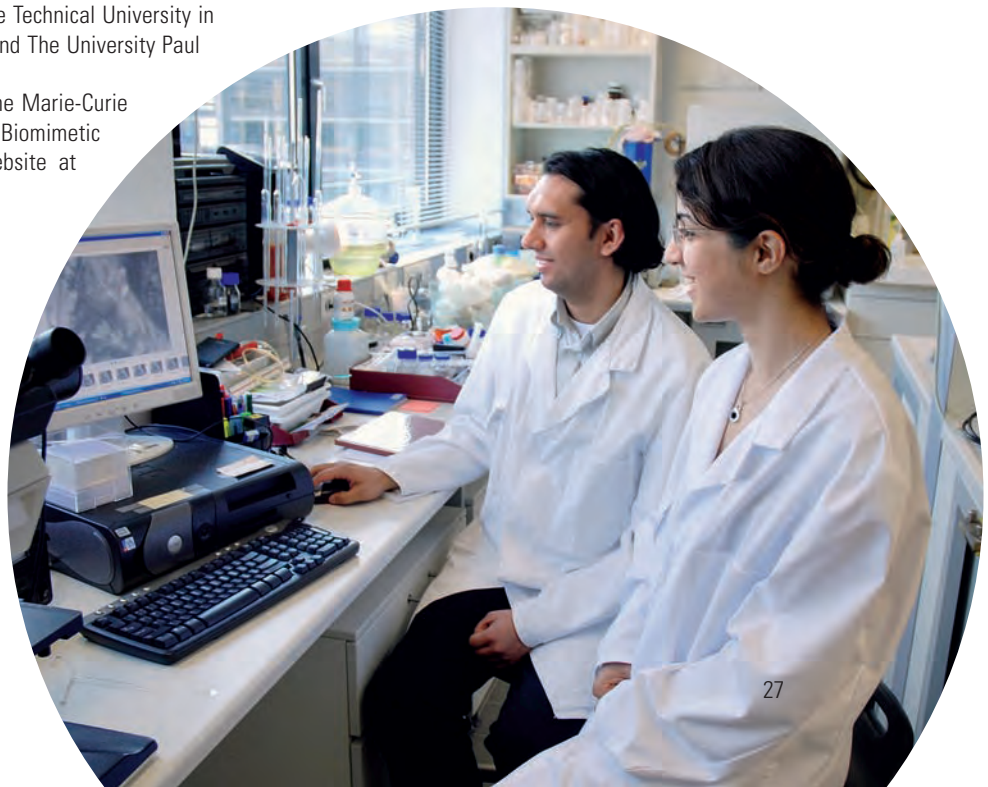
The MPI has already many ongoing cooperations with national and international partners but is always open for new links to new partners. We are particularly interested in those regions where science development is moving at a great pace. That is why we pay great attention to the events in China.

In September/October 2006 we have organized a two-week Summer School on Bio-Systems together with our partners at the CAS. With speakers from Europe, USA and China, the school offered a multidisciplinary overview of biological and biomimetic systems to about 60 masters and PhD Students. For more information, see:
http://www.bio-systems.org/beijing2006

3. Outlook

In the next period of two years, some of the projects will finish and some new projects, conferences and summer schools will be realized. Our graduate program is part of a larger set of activities about bio-systems which is used as an abbreviation of both, biomimetic and biological systems. For more information, see:
www.bio-systems.org.

Reinhard Lipowsky
and Angelo Valleriani



Presse- und Öffentlichkeitsarbeit

Das Max-Planck-Institut für Kolloid- und Grenzflächenforschung informiert innerhalb seiner Presse- und Öffentlichkeitsarbeit über die wissenschaftlichen Innovationen am Institut und deren Ergebnisse in Lehre, Forschung und Anwendung. Auf diese Weise möchten wir ein eigenständiges, positives Image und Vertrauen schaffen. Gleichzeitig soll dazu beigetragen werden eine Brücke von der Lehr- und Forschungsstätte in die Öffentlichkeit zu schlagen, aktuelle Impulse aufzunehmen, neue Ideen zu finden und umzusetzen. 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. Aufmerksamkeit und Interesse für die Wissenschaft und damit letztendlich Akzeptanz, Sympathie und Vertrauen zu gewinnen, sind unsere wichtigsten Anliegen.

Fach- und Publikumsjournalisten werden über das aktuelle Geschehen mit Hilfe von fundierten Nachrichten und Hintergrundwissen informiert. Regelmäßig veröffentlichen wir unseren Zweijahresbericht, Presse-Informationen, beantworten Presseanfragen und halten zu den Medienvertretern persönlichen Kontakt. Neben der klassischen Pressearbeit stellt die Konzeption, Organisation und Durchführung von Veranstaltungen den zweiten Tätigkeitsschwerpunkt des Referats dar. Der alle zwei Jahre stattfindende Tag der Offenen Türen im Wissenschaftspark Golm ist dabei einer unserer Höhepunkte. Gemeinsam mit den Max-Planck-Instituten für Gravitationsphysik und Molekulare Pflanzenphysiologie, den Fraunhofer-Instituten für Angewandte Polymerforschung (IAP) und Biomedizinische Technik (IBMT), dem Golm Innovationszentrum GO:IN sowie der Universität Potsdam bieten wir interessierten Besuchern aller Altersklassen einen faszinierenden Einblick in die Forschung. Das bunte Programm mit Führungen, Experimenten, Vorträgen und Mitmach-Aktionen bietet Jung und Alt Wissenschaft zum Anfassen und bietet zahlreiche Möglichkeiten High-Tech-Technologien hautnah zu erleben und zu begreifen. Der Tag der Offenen Türen wird im Jahr 2007 am 1. September stattfinden.

Zudem werden am Max-Planck-Institut für Kolloid- und Grenzflächenforschung Führungen für Interessierte insbesondere für Schulklassen sowie Vorträge an den Schulen selbst organisiert. Der Internetauftritt des Instituts, aber auch die interne Kommunikation stellen darüber hinaus weitere wichtige Bereiche der Öffentlichkeitsarbeit dar.

Wir sehen es als Aufgabe an, die Bedeutung der Grundlagenforschung und der zukünftigen Entwicklungen in der Kolloid- und Grenzflächenforschung an die breite Öffentlichkeit zu transportieren. Entdecken Sie auf den folgenden Seiten, dass Wissenschaft faszinierend, kreativ und fesselnd ist! Sollten Sie bei auftretenden Fragen unsere Hilfe benötigen, unterstützen wir Sie jederzeit gern.

Katja Schulze
Presse- und Öffentlichkeitsarbeit
katja.schulze@mpikg.mpg.de

Fotos: „Tag der offenen Türen" K. Kreßler, (MPIKG)

Press and Public Relations

Press and 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 and ideas. 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. Attention, interest and finally trust in science must be one of our most important concerns.

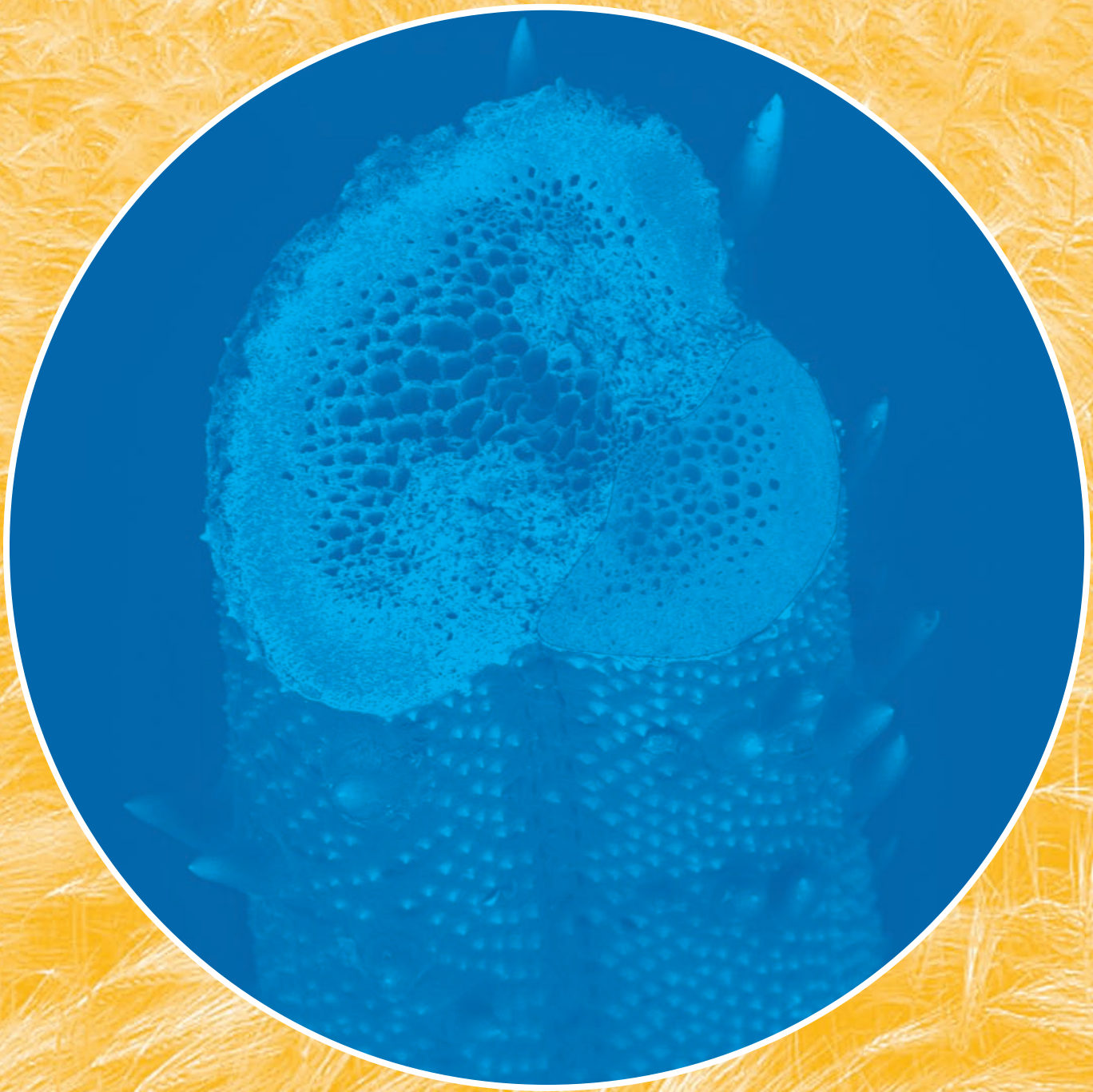
Therefore we inform journalists with profound news and background knowledge about current research. To pursue this task press releases are edited, bro-chures – such as the Biannual Report – are published and distributed on request and informal support is provided whenever necessary. Beside classical Press and 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 2007 will be held together with the Max Planck Institutes of Gravitational Physics and Molecular Plant Physiology, the Fraunhofer Institutes for Applied Polymer Research (IAP) and Biomedical Engineering (IBMT), the Golm Innovation Center GO:IN and the University Potsdam on September 1. There will be lab tours, popular talks and scientific demonstrations providing an excellent opportunity for everybody to experience scientific activity at first hand.

Furthermore tours through the institute as well as talks at schools are organized. But also the internet presence and the internal communication are additional important fields within Press and Public Relations.

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. If you have any further questions, please contact us. We are pleased to help you.

Katja Schulze
Press and Public Relations
katja.schulze@mpikg.mpg.de


BIOMATERIALS



Research in the Department of Biomaterials

Research in the Department of Biomaterials is highly interdisciplinary with a focus on biological and bio-inspired materials. Biological materials constitute most of the body of plants and animals around us. They allow cells to function, eyes to capture and interpret light, plants to stand up to the light and animals to move or fly. Biological structures have always been a source of inspiration for solving technical challenges in architecture, mechanical engineering, or materials science. Nature has developed – with comparatively few base substances, mainly polymers and minerals – a range of materials with remarkable functional properties **[1]**. The key is a complex, often hierarchical structuring of the natural materials **[2]**.

It is not evident that the lessons learned from biological materials will be applicable immediately to the design of new engineering materials. Indeed, **bio-inspiration** is not merely the consequence of an observation of naturally occurring structures. These structures are probably good solutions found by a long adaptation process during evolution, but Nature has to take into account a multitude of boundary conditions (mechanical, biological, related to nutrient supply, etc.) which we hardly know and which might not be important in an engineering context. As a consequence, we have to study carefully the biological system and to understand the structure-function relation of the biological material together with its physical and biological constraints, before it may serve as a model for the design of new materials **[1]**.

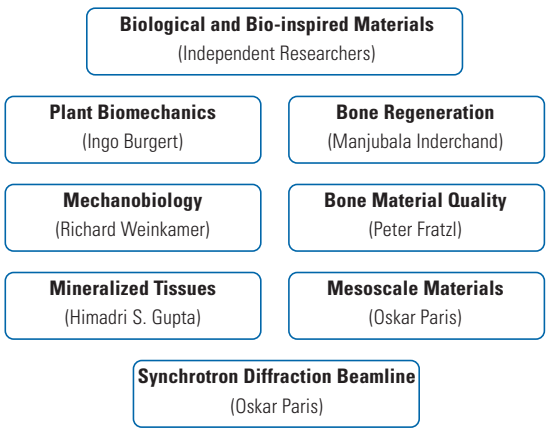


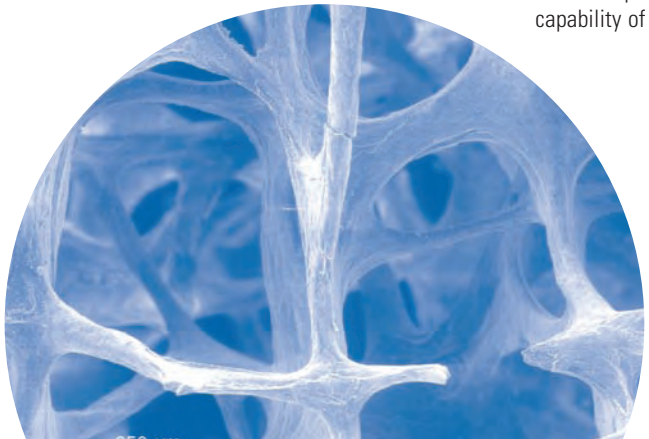
Fig. 1: Research groups in the Department of Biomaterials with respective group leaders

With this paradigm in mind, we have defined the research programme of the Department of Biomaterials as a combination of research on natural tissues and on bio-inspired materials. Accordingly, the Department is organised in several research groups, as shown in **Fig. 1**, and who present their own reports within this volume. In addition, several independent researchers on the postdoctoral level are working on related topics and their reports are summarized jointly in one of the sections (Biological and Bio-inspired Materials).

First, a large effort is devoted to improve our understanding of some biological tissues from a materials science point of view. This requires that we study structure-mechanical function relations, considering the natural environment in which these materials live and grow. One of these tissues is the **plant cell wall**, a composite of (semi-crystalline) cellulose fibrils in an amorphous polymer matrix. This cell wall material has remarkable mechanical properties which may be tuned by the cell over a wide range of stiffness, according to needs, and which is even capable of generating stresses to provide motility. This is described in the reports by Ingo Burgert and by Rivka Elbaum (independent Humboldt Postdoctoral Fellow).

Mineralized tissues are a second example of mechanically outstanding biological materials. Currently, our emphasis is on elucidating the origin of the fracture resistance of bone, not least because of the biomedical importance of this tissue. Most recently, a hierarchical deformation pattern was discovered as a major reason for the mechanical quality of bone tissue (see report by Himadri S. Gupta). These studies are now being extended to deer antler, which is a rapidly growing bone tissue with even higher toughness than bone. The structural origin of the mechanical performance of teeth and the biomineralization of tooth enamel are being addressed by the postdoctoral researchers Paul Zaslansky and Barbara Aichmayer. Their reports are included in the section "Biological and Bio-inspired Materials". Finally, collaborative research on the hierarchical structure and the mechanical properties of glass sponge skeletons is also reported in this same section.

It is 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-



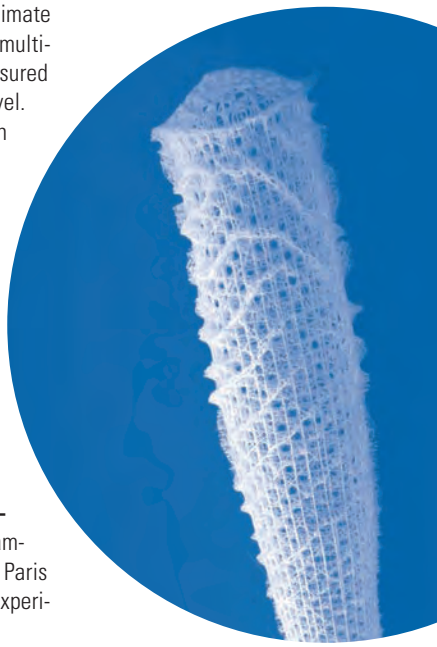
repair. These questions are addressed mostly by theoretical means in the research group on **mechanobiology** (see report by Richard Weinkamer). Moreover, the mechanics of micro-containers and membranes is investigated together with the Interface Department.

In parallel to the study of biological materials, we address topics (right column in Fig. 1) which use the knowledge on biological materials for research either with implications in materials or in biomedical sciences. A major topic is related to **bone material quality** in osteoporosis and its changes with treatment of the disease. This is a long-term collaboration with the Ludwig Boltzmann Institute of Osteology in Vienna, Austria. Recent results obtained in the last two years relate, for example, to bisphosphonate treatment of osteoporosis and of brittle bone disease (osteogenesis imperfecta), see the section on Bone Material Quality.

A further topic with biomedical implications is **bone regeneration**. Bone is among the few tissues in our body which are able to heal and to regenerate completely without leaving a scar. In collaboration with the Charité Medical University and other partners in Berlin and Brandenburg, we are now trying to elucidate the healing process in bone, as well as the physical and biochemical factors which govern it. A new Collaborative Research Center (SFB760) supported by the German Science Foundation, and in which the Department of Biomaterials is heavily involved, is starting in the beginning of 2007. The Department is also member of the Berlin Brandenburg Center for Regenerative Therapies (BCRT) supported by the Ministry of Science (BMBF). Current research is centred on the analysis of the various tissues occurring during bone healing, as well as cell and tissue growth on porous scaffolds, which might serve as implants; see the report by Manjubala Inderchand.

Biomimetic materials are currently developed in one of the research groups, based on thermal and chemical processing of plants. In particular, the processing is studied in detail by in-situ synchrotron diffraction. Further research in this group concerns the behaviour of fluids in mesoporous materials, which are studied in collaboration with partners in Berlin within the framework of the Collaborative Research Center SFB448 (see report by Oskar Paris). Work on bio-inspired active hybrid materials based on gels and microstructured silicon is also conducted in the Department in collaboration with Bell Labs, USA (see section on Biological and Bio-inspired Materials).

Finally, a large effort is devoted to establish **new methods** for analysis of biomaterials. Indeed, studying hierarchical biomaterials requires state-of-the-art experimental equipment and there is also some need for the development of new approaches. One strategy is to set up a suite of scanning imaging methods which may be applied to the same specimen and which give different type of information about the material with a position resolution in the micron range. We are currently using scanning electron microscopy and scanning x-ray diffraction to characterize the micro- and nanostructure. Moreover, we have established Raman imaging to provide information on chemical composition and nano-indentation as well as acoustic microscopy to estimate local mechanical properties. The strength of this multi-method approach is that the different parameters measured on the same specimen can be correlated at the local level. This helps finding structure-property relations even in extremely heterogeneous materials. In-situ techniques are a second type of approach, where we study changes in a material (e.g. due to mechanical stress or to chemical or thermal processing) by time-resolved scattering or spectroscopy during the process itself. In some cases, we can perform such studies in the laboratory (e.g. with Raman or infrared spectroscopy or in the environmental scanning electron microscope), but in many cases we need synchrotron radiation (e. g. for x-ray diffraction or small-angle scattering). A large project in this context is the setting up of a dedicated scanning small- and wide-angle scattering beamline at the **synchrotron** BESSY in Berlin. The end station for this beamline has been developed under the supervision of Oskar Paris (see his report) and is now performing the first user experiments.



Peter Fratzl
Director of the Department
of Biomaterials

[1] Peter Fratzl, Perspective: Biomimetic materials research – What can we really learn from Nature's structural materials? Journal of the Royal Society Interface 2007 (published online).

[2] P. Fratzl and R. Weinkamer, Nature's hierarchical materials, Prog. Mater. Sci. 2007 (in press).

Plant Systems Biomechanics

Ingo Burgert 18.09.1968
1995: Diploma, Wood Science and Technology (University of Hamburg) Thesis: The Fractometer – its potentialities and limits in measuring mechanical properties of living trees
2000: PhD, Wood Science (University of Hamburg) Thesis: The mechanical relevance of rays in the living tree
2000-2003: Postdoc (Institute of Physics and Materials Science, BOKU, Vienna)
Since 2003: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Plant biomechanics provides a powerful tool to gather insights into the relationship of plant form and function as an expression of plant strategy to survive under given environmental conditions and physical constraints. It is also a valuable source for extracting biomimetic principles for the design of new bio-inspired materials (**Fig.1**).

Plants are hierarchically organized which means that their macroscopic properties mainly originate from the nano- and microscale. Nanometer thick semi-crystalline cellulose fibrils embedded in amorphous matrix polymers are the basic assembly of plant cell wall structure. But at these levels of hierarchy, plants manifest a wide variety of adaptable parameters such as cell shape, thickness and arrangement of cell wall layers, the orientation of cellulose microfibrils within cell walls, and in the chemical composition of individual cell wall layers. Micromechanical approaches are well suited to characterize these composite structure for understanding both the material design and the optimization strategies of living plants **[1]**.

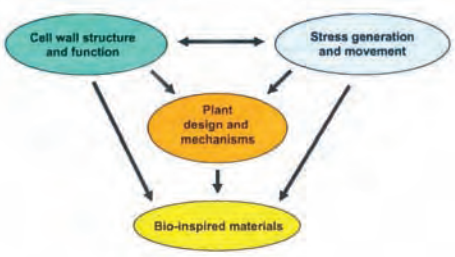


Fig. 1: Schematic of the research interests of the Plant Systems Biomechanics group.

Cell Wall Structure and Function

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 distribution, spatial orientation, and bonding characteristics.

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 hand. The deformation behavior of primary walls was studied by using *Arabidopsis* hypocotyls and was indicative of the crucial role of the cellulose-hemicellulose (xyloglucan) network for stiffness and strength. Cyclic loading experiments on various mutants suggest that the degree of plastic deformation occurring during the first cycle depends on the straightening of the xyloglucan chain.

Cellulose microfibril orientation and matrix interactions in primary cell walls are also of high significance during the course of cell elongation **[2]**. Focusing on the mechanics of cell wall expansion from a plant biomechanics perspective it seems evident that the geometrical constraints imposed by (plastically) inextensible cellulose fibrils have a profound effect on the cell growth behavior. This is less evident at small extensions (up to ~30%) where the fibrils are not yet expected to tilt appreciably into the cell direction (**Fig. 2**).

Most probably, the plastic flow of non-cellulosic matrix dominates the deformation at this stage. For much larger extensions (beyond 100%), the tilting of the cellulose may become important, leading to a stiffening of the cell in its longitudinal direction and compression in its lateral direction. Hence during cell elongation the matrix between cellulose fibrils needs to act in two ways both as a tether during longitudinal extension and later as a spacer when compressed laterally.

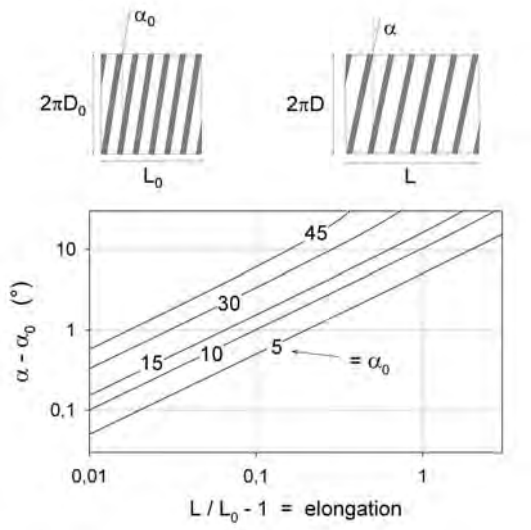


Fig. 2: Change of cellulose orientation as a function of cell elongation in a theoretical model with inextensible cellulose fibrils. The angle of cellulose fibrils with the direction perpendicular to the cell axis is called α (with the value α_0 before elongation). The length of the cell changes from L_0 to L, and its diameter from D_0 to D. The numbers in the figure indicate the cellulose angle α_0 before cell elongation. Both axes are drawn with logarithmic scales [2].

Deformation mechanisms in secondary cell walls were examined with various *in-situ* techniques which simultaneously combine mircomechanical tests with (nano-) structural analysis **[3]**, **[4]**. Tensile tests on mechanically isolated cells **[5]** combined with simultaneous acquisition of Raman spectra have shown that the (stiff) cellulose fibrils carry most of the load with only small and fully elastic deformation **[3]**. Almost all of the deformation takes place by shearing of the (deformable) hemicellulose/lignin matrix. This combination confers both stiffness and toughness to the cell wall.

Enzymatic treatments were utilized to suppress the functioning of individual polymers in the mature cell wall of secondary xylem cells. Micromechanical tests on the modified material revealed the mechanical relevance of hemicelluloses (xylan) in the composite structure.

Stress Generation and Plant Movement

Active movement is usually associated with animals rather than plants. Clearly, plants do not have muscles but they are able to pre-stress their tissues in order to actuate their organs. We showed for normal wood and compression wood of spruce (Picea abies) that either tensile or compressive stresses can be obtained during swelling of the cell wall, depending on the ability of the cell to undergo some torsion **[6]**. This was shown in swelling experiments on individual cells and tissues and can be well understood by simple mechanical considerations taking into account the cell shapes and the observed cellulose fibril orientations (**Fig. 3**).

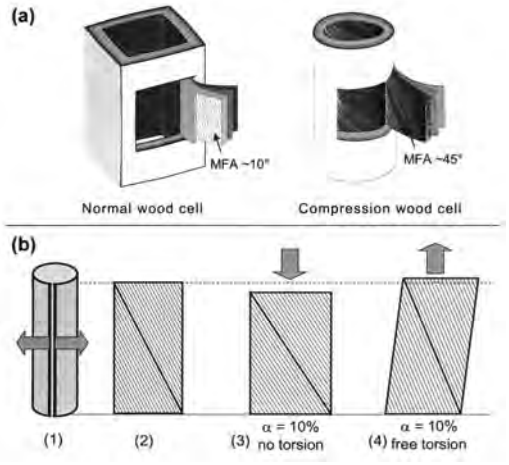


Fig. 3: (a) Schematic drawing of a normal wood and compression wood cell with different cellulose microfibril angles (MFA). (b) Deformation of the cell wall during swelling with inextensible cellulose fibrils (example with microfibril angle = 30°). (1) Cell virtually cut open along a vertical line. (2) Cell wall rolled out indicating the cellulose orientation. (3) Increase of cell wall area (α=10%) due to swelling with inextensible cellulose fibrils and no torsion of the cell. (4) Same when torsion of the cell is allowed [6].

The almost inextensible cellulose fibrils redirect the forces generated by the swelling of the matrix by purely geometrical constraints to produce tension or compression forces according to needs. This principle could be simple enough to be reproduced in artificial systems and one may consider developing fiber-reinforced hydrogels as effective microactuators.

Bio-Inspired Materials

A) Gradients in Plants

Palm trees have evolved gradual transitions between stiff, sclerenchymatous supporting fibres and soft parenchymatous tissue, functioning as a matrix. This structure can help to avoid critical shear stresses and separation of the material at the interfaces when plants are mechanically loaded. Here, we investigated in cooperation with the University of Freiburg (Lab. T. Speck) gradual transitions in arborescent palms at different hierarchical levels by anatomical, micromechanical, physical and biochemical methods taking *Washingtonia robusta* as a model organism **[Fig. 4]**.

The stress-strain curves show a change in cell wall stiffness from the centre to the middle of the fibre cap. The

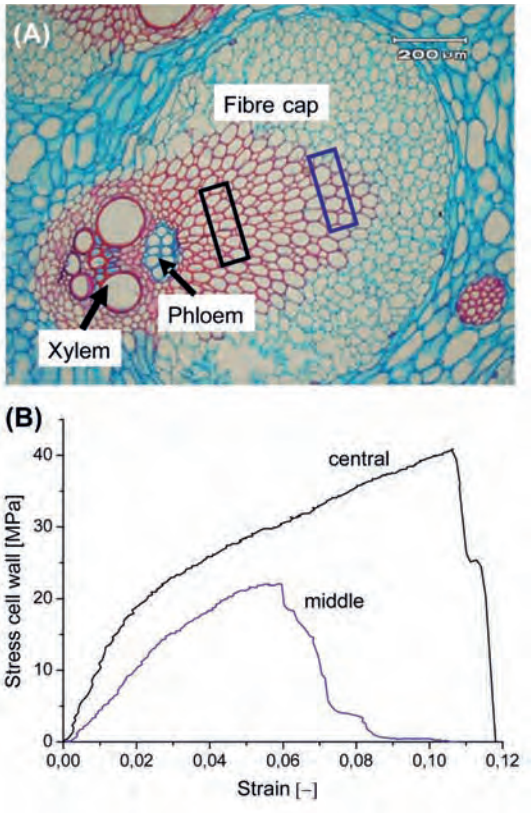


Fig. 4: A) Vascular bundle with xylem, phloem and the fibre cap which can make up to 90 % of the overall bundle area. Fuchsin/chrysoidin/astrablue staining as a qualitative indication of lignification; B) Stress-strain curves of tissues from the central and the middle part of a fibre cap of Washingtonia robusta.

underlying structural and biochemical features are currently studied. Our aim is to transfer the concept of gradual transitions into technical application for innovative structurally optimised composite materials.

Bio-Inspired Materials

B) Fibre-Matrix Interactions

The nanocomposite structure of the plant cell wall with its specific interface design between stiff cellulose fibrils and pliant matrix polymers can be taken as a source of inspiration for a transfer to technical applications. Currently we are running a cooperation project (partners: University of Freiburg (Lab. T. Speck) and ITV Denkendorf) in the framework of the BMBF-Bionik competition on an improvement of technical composites with a new concept for the embedding of glass fibres based on the primary cell wall assembly. With the aid of our mechanical workshop (G. Haseloff) we developed embedding and pull-out test setups to mechanically characterize the interface properties between fibre and matrix.

I. Burgert, W. Abasolo, M. Eder, N. Gierlinger*, L. Goswami, K. Jungnikl, A. Martins, M. Rosenthal, M. Rüggeberg, N. Schreiber, R. Seidel, S. Weichold, K. Yamauchi
ingo.burgert@mpikg.mpg.de

References:

[1] Burgert, I.: Exploring the micromechanical design of plant cell walls. Amer. J. Bot. **93**, 1391-1401 (2006).

[2] Burgert I, Fratzl, P: Mechanics of the expanding cell wall. In: Plant Cell Monogr (5) The Expanding Cell (eds J-P Verbelen, K Vissenberg) Springer-Verlag Berlin Heidelberg, pp.191-215(2006).

[3] Gierlinger, N., Schwanninger, M., Reinecke, A., Burgert, I.: Molecular changes during tensile deformation of single wood fibers followed by Raman microscopy. Biomacromolecules **7**, 2077-2081 (2006).

[4] Thygesen, L.G., Eder, M., Burgert, I.: Dislocations in single hemp fibres – Investigations into the relationship of structural distortions and tensile properties at the cell wall level. Journal of Materials Science **42**, 558-564 (2007).

[5] Burgert, I., Gierlinger, N., Zimmermann, T.: Properties of chemically and mechanically isolated fibres of spruce (Picea abies [L.] Karst.). Part 1: structural and chemical characterization. Holzforschung **59**, 240-246 (2005).

[6] Burgert, I., Eder, M., Gierlinger, N., Fratzl, P.: Tensile and compressive stresses in tracheids are induced by swelling based on geometrical constraints of the wood cell. Planta, DOI 10.1007/s00425-007-0544-9 (2007).

*The APART fellowship (Austrian program for advanced research and technology) of the Austrian Academy of Sciences was awarded to Notburga Gierlinger, who became an independent researcher at the Department in the meantime.

Bone Material Quality and Osteoporosis Research

Peter Fratzl 13.09.1958
1980: Diploma (Ingénieur Diplômé de l'Ecole Polytechnique, Paris)
1983: PhD, Physics (University of Vienna)
Thesis: Investigation of an Al-Zn-Mg alloy using diffuse neutron scattering
1981-1985: Research Scientist (Austrian Academy of Sciences, Vienna; Laboratoire Leon Brillouin, Saclay, France); Visiting Research Fellow (Hahn Meitner Institute, Berlin; New York University)
1986-1998: Assistant and Associate Professor (Institute for Materials Physics of the University of Vienna, Austria)
1988 and 1989: Visiting Professor (Rutgers University, New Jersey, USA)
1991: Habilitation, Solid State Physics (University of Vienna)
Thesis: Precipitation in alloys – small-angle x-ray scattering and computer simulation
Since 1993: Research Associate (Ludwig Boltzmann Institute of Osteology, Vienna).
1993-1994: Visiting Research Fellow (Heriot-Watt University, Edinburgh)
1997: Visiting Professor, (Physics Department of the University of Munich)
1998-2003: Chair of Metal Physics (University Leoben, Austria)
Director (Erich Schmid Institute for Materials Science of the Austrian Academy of Sciences)
Since 2003: Director, Department of Biomaterials (Max Planck Institute of Colloid and Interfaces, Potsdam)
Since 2004: Honorary Professor of Physics at Humboldt University Berlin

References:
[1] D. Dempster, D. Felsenberg, S. van der Geest (Editors): The Bone Quality Book - A Guide to Factors Influencing Bone Strength, Excerpta Medica, Amsterdam (2006); and P. Fratzl: Material properties: mineral cystals. ibidem pp 56-63.

Bone is a hierarchically structured material with remarkable mechanical performance. Understanding its properties is essential for the assessment of diseases such as osteoporosis, for a critical evaluation of current therapies and to aid in their more targeted development. While the full hierarchical structure of bone is extremely complex and variable, its basic building block, the mineralized collagen fibril, is rather universal. The mechanical performance of bone, often coined "bone quality" **[1]**, does not only depend on the shape and the amount of the bone (as estimated by the bone mineral density, BMD), but also on its architecture and on the quality of the bone material. Current research carried out primarily in collaboration with the Ludwig Boltzmann Institute of Osteology (Vienna, Austria) concentrates on studying the structural basis of bone material quality and changes due to disease or treatment.

Anisotropy of Fracture Toughness in Human Compact Bone

Bone material quality depends to a large extent on the orientation of collagen fibrils in bone tissue. In collaboration with H. Peterlik (University of Vienna), we studied controlled crack extension in human femur **[2]**. It was shown that the energy dissipated by the crack is two orders of magnitudes larger if it propagates perpendicularly to the collagen fibrils than when it runs along them. The reason is obvious in **Fig.1**. When the crack follows the main collagen direction, it runs straight and the dissipated energy is low (**Fig. 1B**). In contrast, the crack path is zigzagging when it should run perpendicularly to the collagen direction (**Fig. 1B**), thus dissipating much more energy.

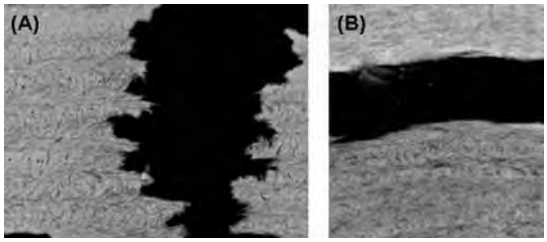


*Fig. 1: Crack propagation in a human femur, perpendicular to the long bone axis (A) and parallel to it (B), from **[2]**.*

Mineral Density in Different Bone Matrices

Since mineral is the stiffer component in bone, it is not surprising that the elastic modulus of the bone matrix depends on the mineral content. **Fig. 2** shows that this dependence is not linear. Even more important, the relation between local elastic modulus (as measured by nanoindentation) and local mineral content (as measured by backscattered electron imaging) depends on the type of organic matrix, for example when one moves from bone into mineralized cartilage in a joint **[3]**.

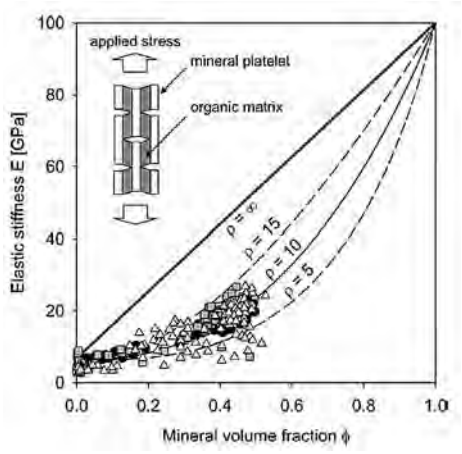


*Fig. 2: Dependence of indentation modulus on mineral content in mineralized cartilage. The lines correspond to a composite model **[3]**.*

Another interesting observation is that bone material quality is also depending on genetic background. A polymorphism affecting a Sp1 binding site in a regulatory region of the COLIA1 gene is known to predispose to osteoporotic fractures by affecting bone strength through mechanisms that are partly independent of differences in bone mineral density (BMD). The bone material in patient biopsies was investigated in collaboration with the University of Aberdeen Medical School **[4]**. Our analysis showed significant reduction in matrix mineralization in bone biopsies from heterozygotes compared with homozygotes (see **Fig. 3**).

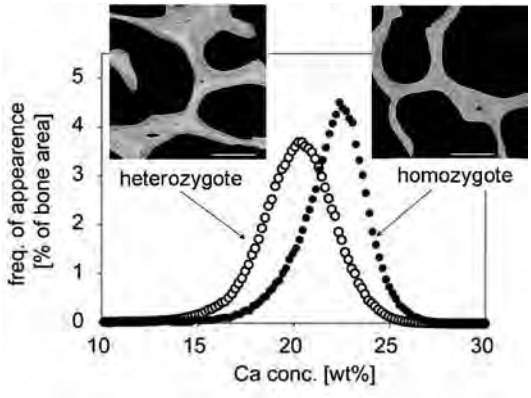


*Fig. 3: histogram of mineral density distribution in trabecular bone matrix of biopsies from patients with a polymorphism in the COLIA1 gene **[5]**.*

Raman Imaging of Bone

A considerable effort was undertaken by Murat Kazanci (postdoc) to establish Raman imaging as a tool for studying bone material quality. The reason for the interest in this technique is that it allows the imaging of material parameters with one micron spatial resolution and spectral resolution much better than infrared spectroscopy. The Raman signal from compact bone turned out to be extremely sensitive to tissue orientation (**Fig. 4**) and methodology was devised to

determine the amounts of mineral and protein in the matrix, as well as some information on their orientations **[5]**.

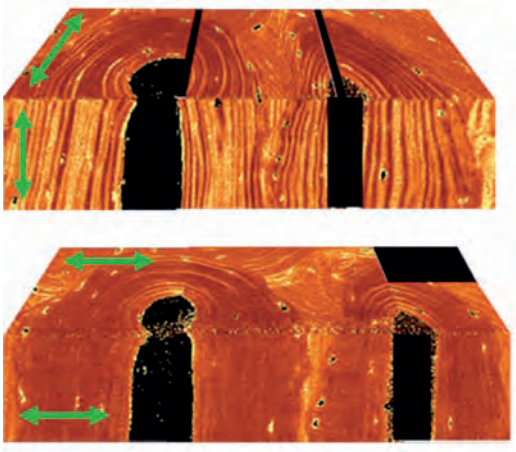


Fig. 4: Ratio of the $\nu_1 PO_4$ to the amide I band in two osteons within human cortical bone (collaboration with HD Wagner, Weizmann Institute, Israel). The dark channels in the figures are blood vessels in the centre of osteons. The image of the bone tissue depends strongly on the polarization of the laser beam (green arrows).

Bone Quality in Osteoporosis Treatment

Osteoporosis is a common disease associated with reduced bone mass and increased bone fragility. Bone is constantly turned over by specialized bone cells, osteoclasts which resorb bone and osteoblasts which form new bone. The reduction in bone mass in osteoporosis is linked to an imbalance between these two processes. As a consequence, treatment strategies are typically targeting either the osteoclasts to reduce bone resorption or the osteoblasts to increase bone formation. Bisphosphonates are used in this context as antiresorptive drugs. In collaboration with Procter and Gamble Pharmaceuticals (Ohio, USA), we studied the effects of osteoporosis treatment on bone material quality in a clinical trial. Biopsies from patients treated with the bisphosphonate risedronate for three and five years were studied using backscattered electron imaging **[6]** and infrared spectroscopy **[7]**. The main result was that the mineral content of the bone matrix was increased by the treatment, without any further visible modifications at the material level.

The effects of a therapy with parathyroid hormone (PTH), known to induce bone formation, combined with osteoprotegerin (OPG), known to act on bone resorption, was explored in an animal study, in collaboration with AMGEN Inc (Thousand Oaks, Canada). It was found that PTH was responsible for an increase in bone volume, whereas OPG positively influenced the homogeneity and density of mineralization without affecting the nanostructure of the bone material **[8]**.

Bisphosphonate Treatment of Brittle Bone Disease

Brittle bone disease (osteogenesis imperfecta, OI) is a disorder which is linked to genetic modifications of the collagen gene and which leads to enhanced bone fragility. Children with this disease suffer from multiple fractures and associated complications. It is known that the fracture incidence in patients can be reduced by a treatment with bisphosphonates. It is not known, however, in which way this treatment affects the bone quality and leads to a reduction of bone fragility. In collaboration with the Hospital for Special Surgery (New York, USA), we studied a mouse model of this disease treated with the bisphosphonate alendronate (ALN). It was found that ALN augmented the mechanical, geometrical, and material properties of cortical and trabecular bone in controls, while the only observable improvement to the OI mouse model was increased bone volume **[9]**, see **Fig. 5**.

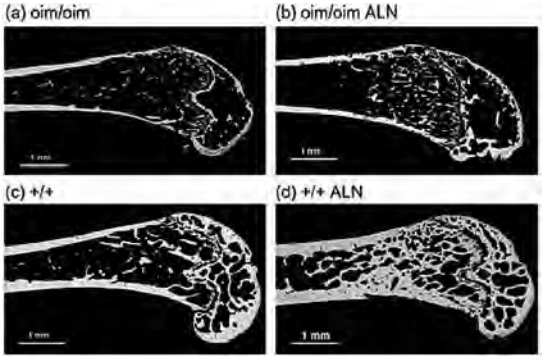


*Fig. 5: Backscattered electron images of longitudinal views of femora from untreated and ALN-treated bone from the OI mouse model (a, b) and controls (c, d), **[10]**.*

This work was continued by studying biopsies from young OI patients treated with the bisphosphonate pamidronate (PAM), in collaboration with the Shriners Hospital for Children and McGill University (Montreal, Canada) **[10]**. While the OI bone tissue was found stiffer and more mineralized than controls, the anti-fracture effectiveness of PAM treatment was primarily due to an increase of bone volume (see **Fig. 6**). This result is very similar to what was found for the animal model.

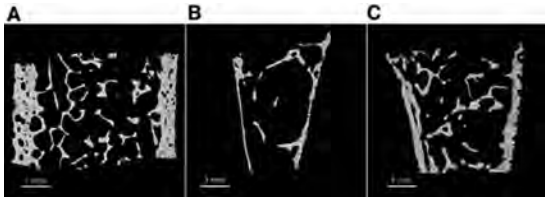


*Fig. 6: Back scattered electron images of transiliac bone biopsies, from (A) age-matched control, (B) a 6 year-old girl with OI type III caused by a mutation in the COL1A1 gene, and (C) the same patient after 2.8 years of PAM treatment **[10]**.*

P. Fratzl, M. Kazanci (Postdoc), mainly in collaboration with the Ludwig Boltzmann Institute of Osteology, Vienna, Austria (P. Roschger, E.P. Paschalis, K. Klaushofer, and others)
Fratzl@mpikg.mpg.de

[2] H. Peterlik, P. Roschger, K. Klaushofer, P. Fratzl: From brittle to ductile fracture of bone. Nature Materials **5**, 52-55 (2006).
[3] H. S. Gupta, S. Schratter, W. Tesch, P. Roschger, A. Berzlanovich, T. Schoeberl, K. Klaushofer and P. Fratzl: Two different correlations between nanoindentation modulus and mineral content in the bone-cartilage interface. J. Struct. Biol. **149**, 138 - 148 (2005).
[4] T.L. Stewart, P. Roschger, B.M. Misof, V. Mann, P. Fratzl, K. Klaushofer, R. Aspden, S.H. Ralston. Association of COLIA1 Sp1 alleles with defective bone nodule formation in vitro and abnormal bone mineralization in vivo. Calcif. Tissue Int. **77**, 113-118 (2005).
[5] M. Kazanci, P. Roschger, E. P. Paschalis, K. Klaushofer, P. Fratzl: Bone osteonal tissues by Raman spectral mapping: orientation-composition. J. Struct. Biol. **156**, 489-96 (2006).
[6] R. Zoehrer, P. Roschger, E.P. Paschalis, J.G. Hofstaetter, E. Durchschlag, P. Fratzl, R. Phipps, K. Klaushofer: Effects of 3- and 5-years treatment with risedronate on bone mineralization density distribution in triple biopsies of the iliac crest in postmenopausal women. J. Bone Miner. Res. **21**, 1106-1112 (2006).
[7] E. Durchschlag, E.P. Paschalis, R. Zoehrer; P. Roschger; P. Fratzl; R. Recker; R. Phipps; K. Klaushofer: Bone material properties in trabecular bone from human iliac crest biopsies after 3- and 5-year treatment with risedronate. J. Bone Miner. Res. **21**, 1581-1590 (2006).
[8] A. Valenta, P. Roschger, N. Fratzl-Zelman, P.J. Kostenuik, C.R. Dunstan, P. Fratzl, K. Klaushofer: Combined treatment with PTH and OPG increases bone volume and uniformity of mineralization in aged ovariectomized rats. Bone **37**, 87-95 (2005).
[9] B.M. Misof, P. Roschger, T. Baldini, C.L. Raggio, V. Zraick, L. Root, A.L. Boskey, K. Klaushofer, P. Fratzl, N.P. Camacho: Differential effects of alendronate treatment on bone from growing osteogenesis imperfecta and wild-type mouse. Bone **36**, 150-158 (2005).
[10] M. Weber, P. Roschger, N. Fratzl-Zelman, T. Schöberl, F. Rauch, F.H. Glorieux, P. Fratzl, K. Klaushofer: Pamidronate does not adversely affect bone intrinsic material properties in children with osteogenesis imperfecta. Bone **39**, 616-622 (2006).

Mineralized Tissues

Himadri Shikhar Gupta 26.06.1973
1991-1996: M.Sc. in Physics (Indian Institute of Technology, Kanpur, India)
1996-2000: PhD, Physics (Rutgers University, New Jersey, USA)
Thesis: Phase Segregation and Alloying in Ni-base Superalloys: Models and Experiments
2000-2003: Postdoctoral Research, (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, Germany)

Our research looks at the structural adaptation of mineralized tissues to their mechanical function at the length scale of a micron and below. At this level, the extracellular connective matrix in both vertebrate and invertebrate organisms often consists at the molecular level of a composite where organic molecules (such as collagen or chitin) are interpenetrated with inorganic crystallites (typically calcium phosphates or carbonates) to form an anisotropic, hard and tough material. Weight for weight, such biomineralized tissues compare favorably with man-made composites, although requiring much lower temperatures and processing conditions. Therefore, an understanding of the structural design principles in such biomaterials may provide guidelines in making new strong composite materials. In addition, understanding how perturbations in the mineralized microstructure affect mechanics (in bone diseases like osteoporosis) would be important in developing treatments for such pathological conditions.

Bone consists of a compact tissue type (cortical bone) and a spongy, porous material (trabecular bone). In both tissue types, the basic building block is the bone lamella, typically about 5 µm thick. In cortical bone, lamellae form laminated cylindrical composite structures built around blood vessels, which are denoted as secondary osteons. While understanding the internal architecture of such osteons is crucially important for bone biomechanics, a convincing and quantitative structural model has thus far been elusive. Using a novel combination of high brilliance synchrotron radiation with a micron-sized beam and local crystallographic texture measurements **[1]**, we were able to show that the collagen fibers are arranged in layers of varying helical pitch with respect to the osteon long axis, in effect forming a right handed spiral motif (**Fig. 1**) **[2]**. Such a spring like structure would be capable of absorbing elastic energy during physiological motion, and may act as a buffer preventing microcracks from penetrating to and destroying the sensitive inner blood vessel.

Using a combination of scanning microprobe methods (nanoindentation and backscattered electron microscopy) we were able to further elucidate the mechanical structure of the osteon. We showed that it consists of layers of alternating high and low stiffness within a single lamella and that the layers of lower modulus correspond to regions of lower average mineral content **[3]**. Such a compositionally and mechanically modulated structure is an example of a functionally graded material, and would act as an excellent crack stopper, as has been demonstrated theoretically.

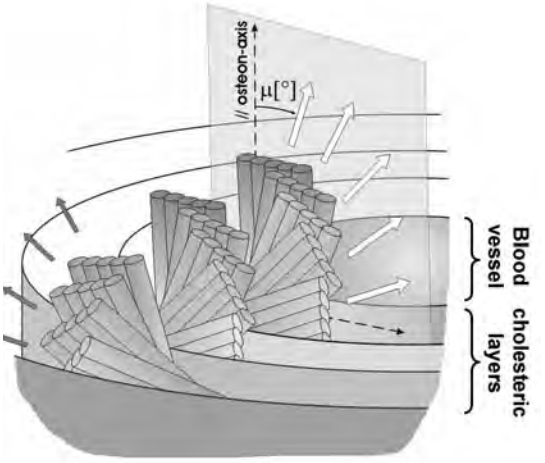


Fig. 1: Right handed spiral twisting of the fiber orientation in compact bone lamellae. The orientation of the fibrils changes with a periodicity of a single lamellar width (~ 5 µm). The last lamella between the osteon and the enclosing interstitial bone has the opposite chirality.

The bone lamellae are comprised of mineralized collagen fibrils, which are 100 to 200 nm diameter composites of type I collagen and hydroxyapatite mineral embedded in a small amount of extrafibrillar matrix. Using *in-situ* mechanical testing with time-resolved synchrotron X-ray diffraction, we showed that the fibrils in bone take about half the total deformation in the tissue under tensile load, and do not stretch further in the inelastic regime. Based on these findings, we proposed a fibril level model of interfibrillar shearing, where the total strain is divided into a tensile component carried by the fibrils and shearing in the thin layers of extrafibrillar matrix (~ a few nm thick) between them (**Fig. 2**) **[4]**. Above the mechanical yield point, a stick-slip mechanism of interfibrillar sliding results **[5]**, which leads to a large work of fracture.

To understand the way strain is transferred down the structural hierarchy, a novel combination of tensile testing of single fibrolamellar bone packets with wide-angle synchrotron X-ray diffraction and small angle X-ray scattering was used. This technique enables us to measure, concurrently, the strain in the tissue, the fibrils and the mineral particles. UV-laser microdissection enabled the isolation of single bone packets at the tissue level, excluding all structures at higher length scales in the hierarchy. Strain is passed down in successively lower fractions from the tissue down to the molecular level (**Fig. 3**) **[6]**, via shearing strains in the intervening extra- and intrafibrillar organic matrix, and depends on the degree of hydration of the organic matrix. Such an arrangement results in a high stiffness of the overall material while protecting the brittle hydroxyapatite phase from excessive load.

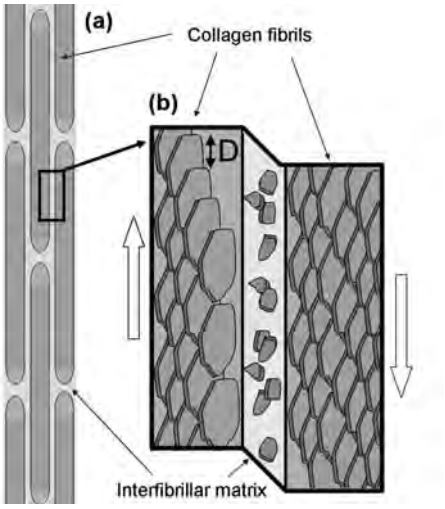


Fig. 2: Shearing model of interfibrillar deformation in bone. White arrows denote the direction of relative motion of fibrils under tensile stress. The interfibrillar matrix may be also partially mineralized.

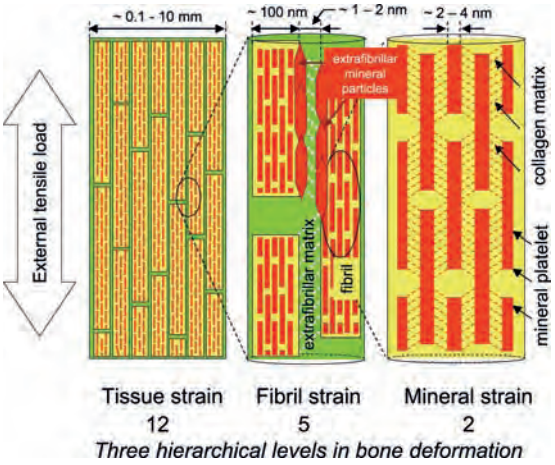


Fig. 3: Hierarchical deformation in bone at three different levels: tissue, fibril and mineral particle. Red hexagons denote extrafibrillar mineral particles, and dashed lines the direction of (possibly inhomogeneous) shear in the matrix between stiff elements.

Using a thermally activated stress flow analysis originally developed to study plastic deformation in metals, we established that the fundamental molecular step in plastic deformation of bone takes place in a volume of about 1 nm^3, and requires activation energy of about 1 eV. Based on the magnitude of these quantities, a model for bone fracture was proposed, where breakage of ionic bonds (in the extrafibrillar matrix) between long irregular polyelectrolyte chains and divalent ions like calcium mediate bone plasticity (**Fig. 4**) **[7]**. Modifying or altering the properties of this extrafibrillar "glue" could be an effective way to tune the properties of bone, and is a current focus of our research.

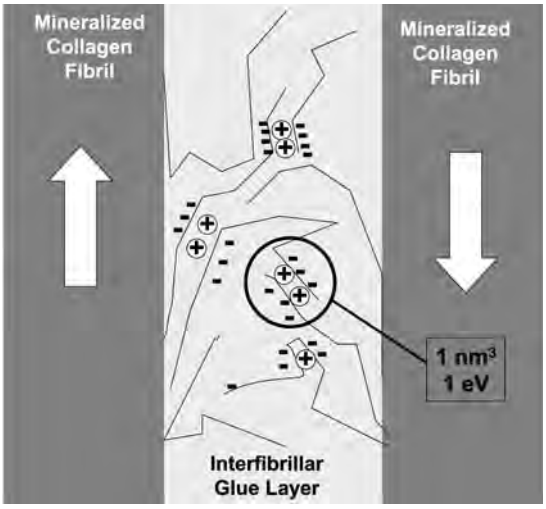


Fig. 4: Ionic bond breaking between divalent ions and polyelectrolyte molecules in the extrafibrillar matrix mediates bone plasticity. Circles denote cations (like calcium) and irregular lines denote polyelectrolytes (noncollagenous proteins like osteopontin or fetuin, or proteoglycans)

Synchrotron studies of the fibrillar deformation mechanisms of the organic collageneous matrix of bone revealed that the unmineralized collagen fibrils in bone deform essentially elastically, and take up only 1/4 - 1/2 of the total tissue strain **[8]**. Antler tissue, a truly striking example of a bone-like hard tissue which is extremely tough, is being investigated by both *in-situ* and scanning microprobe methods to reveal the origins of its excellent toughness.

H. S. Gupta, P. Fratzl, K. Kanawka, S. Krauß, P. Leibner, J. Seto, U. Stachewicz, W. Wagermaier
Himadri.Gupta@mpikg.mpg.de

References:

[1] Wagermaier, W., Gupta, H. S., Gourrier, A., Paris, O., Roschger, P., Burghammer, M., Riekel, C. and Fratzl, P.: Scanning texture analysis of lamellar bone using microbeam synchrotron X-ray radiation. J. Appl. Cryst., **40**, 115-120 (2007).

[2] Wagermaier, W., Gupta, H. S., Gourrier, A., Burghammer, M., Roschger, P. and Fratzl, P.: Spiral twisting of fiber orientation inside bone lamellae. Biointerphases, **1**, 1-5 (2006).

[3] Gupta, H. S., Stachewicz, U., Wagermaier, W., Roschger, P., Wagner, H. D. and Fratzl, P.: Mechanical modulation at the lamellar level in osteonal bone. J. Mater. Res., **21**, 1913-1921 (2006).

[4] Gupta, H. S., Wagermaier, W., Zickler, G. A., Aroush, D. R. B., Funari, S. S., Roschger, P., Wagner, H. D. and Fratzl, P.: Nanoscale deformation mechanisms in bone. Nano Lett., **5**, 2108-2111 (2005).

[5] Gupta, H. S., Wagermaier, W., Zickler, G. A., Hartmann, J., Funari, S. S., Roschger, P., Wagner, H. D. and Fratzl, P.: Fibrillar level fracture in bone beyond the yield point. Int. J. Fract., **139**, 425-436 (2006).

[6] Gupta, H. S., Seto, J., Wagermaier, W., Zaslansky, P., Boesecke, P. and Fratzl, P.: Cooperative deformation of mineral and collagen in bone at the nanoscale. Proc. Natl. Acad. Sci., **103**, 17741-17746 (2006).

[7] Gupta, H. S., Fratzl, P., Kerschnitzki, M., Benecke, G., Wagermaier, W. and Kirchner, H. O. K.: Evidence for an elementary process in bone plasticity with an activation enthalpy of 1 eV. J. Roy. Soc. Interface, doi:10.1098/rsif.2006.0172, published online (2006).

[8] Kanawka, K.: Diploma Thesis, Max Planck Institute of Colloids and Interfaces (2006).

Bone Regeneration

Inderchand Manjubala 07.02.1974
1996: M.Sc., Physics
(University of Madras, India)
Thesis: Synthesis and Characterisation of functional gradient materials using Indian Corals
1997-2002: Ph.D., Physics-Biomaterials
(University of Madras, India)
Thesis: Development and Evaluation of resorbable biphasic calcium phosphate ceramics as bone replacement materials
2002-2003: Postdoc
(Institute of Materials Science and Technology, University of Jena, Germany)
2004-2005: Postdoc (Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2006: Group Leader (Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam)

Our group deals with two different approaches on similar themes of bone and tissue regeneration.

The first aim is to understand the processes underlying the new bone tissue formation in-vitro both by physical and biological approaches. A biomaterial scaffold is used as a template to analyze the behavior of the pre-osteoblastic bone cells to produce new bone-like tissue.

The second aim is to acquire more knowledge on the properties of the tissues formed during bone healing process which could lead to understand the mechano-regulation of the biological process during fracture healing, by the application of our multi-method approach. Further this multi-method approach is applied to study the quality of the bone material in bone biopsies related to bone diseases and their treatment. The project of fracture healing has started this year within the framework of Sonderforschungbereich (SFB) 760 focused in Berlin with research partners from Charité-Universitätsmedizin Berlin, GKSS Institute for Polymer Research at Teltow.

New Bone Tissue Formation *in-vitro*

(A) Bone Replacement Scaffolds via Rapid Prototyping

An ideal scaffolding material for bone tissue engineering should replicate the bone anatomy at microscopic level with interconnected micro and macro pores and with a similar composition of nanocomposite and should be able to promote the osteoblast proliferation and expression of the osteoblastic phenotype. Solid freeform fabrication or rapid prototyping (RP) is a technology by which a complex three dimensional (3D) structures can be produced directly from computer generated (CAD) design. CAD and RP together can be used to control the macro and micro-architecture of porous scaffolds. Two different types of rapid prototyping methods were used suitable to produce ceramic and polymer composite scaffolds respectively. A rapid prototyping system based on "Digital Light Processing" called Envisiontec Perfactory Mini (Envisiontec, Germany), was used for resin molds and a 3D wax printer, Solidscape Modelmaker II (Solidscape, USA) was used to produce wax molds. We aim at developing a hydroxyapatite and a polymeric composite scaffold with defined internal architecture by RP method. Sintered dense hydroxyapatite scaffolds were produced using resin molds by slurry casting method and characterized **[1,2]**. To mimic the components of bone, a biopolymer such as chitosan is used in combination with apatite to form a composite scaffold. Chitosan has been proposed to serve as a non-protein matrix for three-dimensional tissue growth, a potential candidate for tissue engineering and drug delivery systems. The composite scaffolds are produced using dissolvable wax moulds and then freeze dried and cross-linked to produce micro pores to enhance vascularisation in the scaffolds **[3]**.

Cell attachment, proliferation and differentiation over time on a material are indication of cellular compatibility of the material and determine the suitability of the material for tissue engineering application. The fabricated hydroxyapatite and chitosan/apatite scaffolds were accessed for their biocompatibility with bone cells using pre-osteoblastic cell line. The cells cultured on scaffolds proliferated over the material and pores in multilayer and produced extra-cellular matrix in 3 weeks, as seen from histological staining (**Fig. 1**). The structure of the scaffold allows more cells to grow compared to two-dimensional matrices **[3]**.

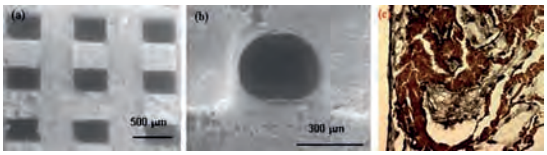


Fig. 1: Electron micrographs of (a) cross-section of chitosan-apatite scaffold, (b) cells covering the pore channel in a circular fashion and (c) Gömöry staining reveals the formation of an extracellular matrix consisting of collagen.

Additionally, the effect of additional factors such as osteogenic hormones and growth factors on the proliferation and differentiation of the cells in scaffolds are investigated **[4]**.

(B) Tissue Growth on Biomaterials of Controlled Geometry and Stiffness

Bone regeneration is influenced by biochemical, biomechanical as well as cellular mechanisms. On the level of single cells, it is well investigated that initial cell attachment and following cell spreading and proliferation is determined by surface topography at the nano- and micrometer scale. But beyond those levels, cells have developed highly sophisticated and active mechanisms to probe their environment. Physical parameters of supports, such as scaffolds, may also have an impact on cell amplification and furthermore, on tissue formation.

For this purpose we established a model system, which allowed in parallel microscopic observation as well as quantification of new tissue formation in a thee-dimensional environment. We used thee-dimensional hydroxyapatite plates containing channels of various shapes (triangular, squared, hexagonal and round) and three various sizes. These hydroxyapatite plates were produced via rapid prototyping method mentioned earlier. Tissue formation occurs in that way, that, independent form the original shape, the new formed tissue keeps a round central canal.

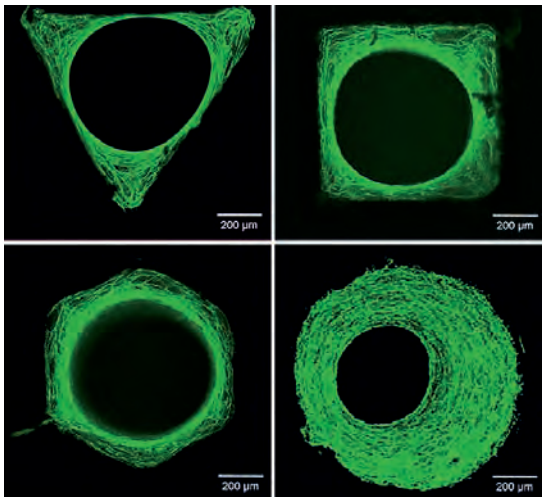


Fig. 2: Extracellular matrix (ECM) tissue growth in 3D channels of various shapes showing that the growth is independent of shape and forms a round central channel.

This amplification modus is maintained throughout the whole tissue into the depth of the channels, observed with confocal laser scanning microscopy (**Fig 2**). Following the kinetics of tissue formation over of period of six weeks showed no shape dependence of the amount of tissue area, but revealed strong size dependence. In that process the development of mechanical forces within the tissue itself may play a key role in growth behavior. Thus, tissue formation in vitro is also determined by physical properties. Additional to the native conditions, nanomodifications of the surface with proteins, which enhance attachment and are involved in the differentiation process of osteoblasts, especially RGD-peptides, will be used to guide the differentiation of osteoblasts.

Apart from investigating tissue formation in 3D matrices, we also studied the role of individual components of the cells during differentiation and proliferation by physical methods such as X-ray scattering and Fourier transform infrared microscopy and spectroscopy.

Characterisation of Bone Healing and Bone Regeneration Processes

Bone healing is a complex process in which different types of tissue are being formed and remodeled. While the pathological evaluations describe the spatial and temporal distribution of the various tissue types comprising the callus (**Fig 3**), little is known of their material properties. In addition, the patterns of appearance of these tissue types as well as their physical properties depend both on biological factors and physical influences, such as mechanical stress. A better understanding of the mechano-regulation of the biological processes during healing requires more knowledge on the properties of the tissues making up the callus. We investigate the spatial distribution and temporal sequence of ultrastructure and mechanical properties of callus tissues over the course of bone healing **[5]**. We apply our established multimethod approach, whereby the same specimen is scanned to map tissue composition, mineral particle size and concentration, as well as mechanical properties at the local level with micrometer resolution, using scanning small- and wide-angle x-ray scattering, scanning electron microscopy, Raman imaging, nanoindentation and acoustic microscopy.

Furthermore, understanding the bone healing process not only in the native state, but also under the influence and intervention of biological factors or physical stimuli on callus tissue formation, is necessary to evaluate the clinical conditions of fracture healing. This project is in close conjunction with the researchers at Charité-Universitätsmedizin Berlin, where the bone healing experiments is carried out in both small and large animal models, as it is known that the tissue architecture is quite different in different animal species.

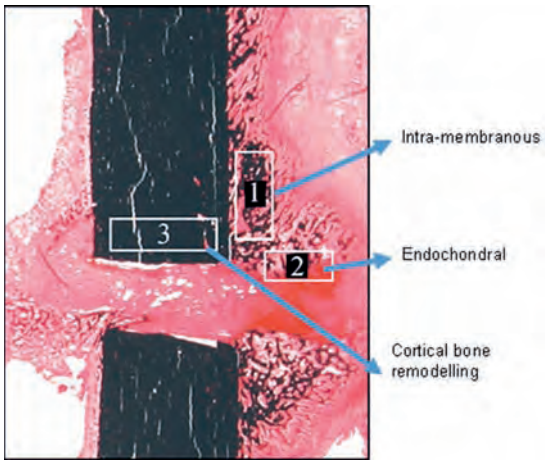


Fig. 3: The various tissues formed during fracture healing identified by histology. The material properties of these tissues are still unknown.

Bone Material Quality Related to Diseases and their Treatment

The changes occurring in bone material quality with respect to disease and their treatment is studied in close collaboration with the researchers at Ludwig Boltzmann Institute of Osteology in Vienna, Austria. The project deals with understanding the correlation of nano mechanical and nano-structural properties of diseased bone in relation to mineral content and treatment parameters in significant bone diseases such as osteoporosis and osteolathyrism. The methodologies used are quantitative back-scattered electron imaging (qBEI), scanning nanoindentation and small-angle x-ray scattering techniques

I. Manjubala, P. Fratzl, C. Lange, L. Li, C. Pilz, M. Rumpler, A. Woesz
i.manjubala@mpikg.mpg.de

References:

[1] Woesz, A., Rumpler, M., Manjubala, I., Pilz, C., Varga, F., Stampfl, J., Fratzl, P.: The Influence of the Thermal Treatment of Hydroxylapatite Scaffolds on the Physical Properties and the Bone Cell Ingrowth Behaviour. Mater. Res. Soc. Symp. Proc. **874**, L.7.9.1 (2005).

[2] Woesz, A., Rumpler M., Stampfl, J., Varga, F., Fratzl-Zelman, N., Roschger, P., Klaushofer, K., Fratzl P.: Towards bone replacement materials from calcium phosphates via rapid prototyping and ceramicgelcasting. Mater.Sci. Eng.C **25**,181(2005).

[3] Manjubala, I., Woesz, A., Pilz, C., Rumpler, M., Fratzl-Zelman, N., Roschger, P., Stampfl, J., Fratzl, P.: Biomimetic mineral-organic composite scaffolds with controlled internal architecture. J. Mater. Sci. Mater. Med. **16**, 1111 (2005).

[4] Rumpler, M., Woesz, A., Varga, F., Manjubala, I., Klaushofer, K., Fratzl, P.: Three-dimensional growth behaviour of osteoblasts on biomimetic hydroxylapatite scaffolds. J. Biomed. Mater. Res.A: 81A, 40 (2007).

[5] Manjubala, I., Epari, D.R., Duda, G.N., Fratzl, P.: Micro-mechanical property of fracture callus in healing bone. Abstract in Calcified Tissue Int. **78**, S58 (2006).

Mechanobiology

Richard Weinkamer 14.08.1967
1995: Diploma, Mathematics (University of Vienna)
Thesis: The modular group: an investigation with methods of combinatorial group theory
1998: Research Stay (Rutgers University, New Jersey)
2000: PhD, Physics (University of Vienna)
Thesis: Diffusion and diffusional phase transformations in binary alloys: Monte Carlo simulations of lattice models
2000-2003: Postdoc, Staff Scientist (Erich Schmid Institute of Materials Science, Leoben)
Since 2003: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Mechanical forces play a crucial role for the performance of biological and chemical systems. Mechanobiology studies how mechanical forces control the development and maintenance of living tissues and how their structure adapts to changes in the mechanical environment. Computational approaches have proven successful in gaining insight into the relation between local rules describing the action of living cells and global changes in the structure. The aim of our work on the mechanobiological system of trabecular bone is to understand the relation between the processes of remodeling and mineralization and its effect on the structure at two different hierarchical levels: trabecular architecture and bone material.

The applicability of man-made micro-capsules depends strongly on a control of their mechanical properties. We have studied the interplay between mechanics and chemistry for capsule systems made of catanionic amphiphilic molecules and polyelectrolytes.

Trabecular Bone: Architecture

Living trabecular bone is continuously remodeled by the resorption and deposition of bone packets. The probability for deposition is increased (decreased) at sites with a high (low) mechanical loading. A crucial unknown for a deeper understanding of the remodeling process is the phenomenological remodeling rule at the core of the controlling feedback loop (**Fig. 1**): it relates the local mechanical stimulus to the probability for bone resorption/deposition at the bone surface. We developed a computer model, which allows the implementation of different remodeling rules, and studied their effect on the trabecular architecture (**Fig. 1**) and its time evolution **[1]**. In our simulations we found features that are independent of the remodeling rule, e.g., the emergence of a network-like structure and the coarsening of the structure by a reduction of the number of trabeculae and thickening of the remaining ones, while the bone volume fraction remained constant **[2,3]**. Strongly dependent on the remodeling rule are architectural parameters like the bone surface roughness, the velocity with which coarsening of the structure proceeds and the response of the system to external perturbations. An example is given in **Fig. 1** where the probability for bone resorption was varied, a parameter accessible by present-day medications. Depending on the implemented remodeling rule, this variation has either almost no or a significant effect on the resulting bone volume fraction. Comparison with real bone lead us to the conclusion that in real bone a remodeling rule with an activation threshold for the bone depositing cells similarly to the step-remodeling rule of **Fig.1** is active **[3]**.

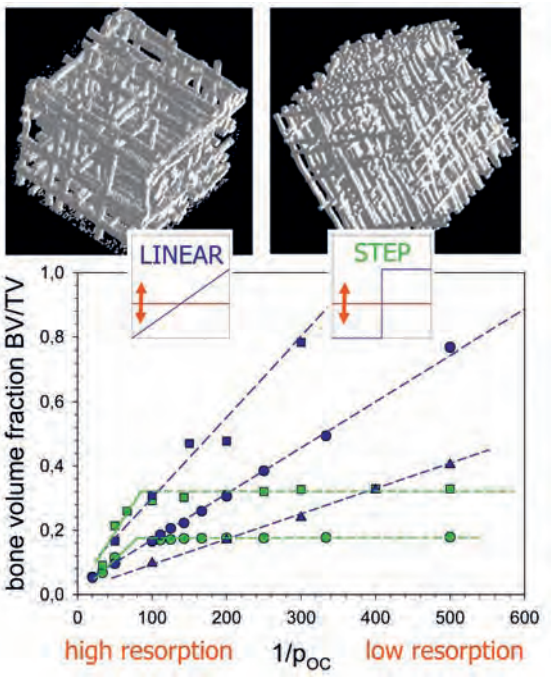


Fig. 1: Comparison between two different remodeling rules for bone remodeling: linear, which assumes a linear relationship between mechanical stimulus and bone deposition probability and step, which assumes a step function for this relation (blue lines in the small insets); on top the resulting microstructure for the two different remodeling rules. The plot below shows the response of the simulation model to changes in the activity of bone resorbing cells for a linear remodeling rule with different slopes (different blue symbols) and a step-remodeling rule with different step position (different green symbols).

Trabecular Bone: Material

At the material level, trabecular bone consists of a patchwork of bone packets with different mineral content. This structure is the result of remodelling and a process of mineralization, which leads to a temporal increase of the mineral content in the initially unmineralized bone packet. The heterogeneity of the mineral content is usually characterized by a frequency distribution, the bone mineralization density distribution (BMDD). For healthy humans, experiments demonstrated that the bell-shaped BMDD (**Fig. 2**) is almost unchanged during life time. With a theoretical model, which considers both processes, remodeling and mineralization, we could connect the shape of the BMDD with the mineralization law, which describes the increase of the mineral content with time in a single bone packet. For the mineralization law in healthy humans our model predicts a rapid increase in the mineral content up to more than 50% of the total capacity followed by a much slower phase which extends over several years **[4]**. An important application of the model is to predict the time evolution of the BMDD due to changes in the turnover. Some bone diseases, the most prominent being osteoporosis, are connected with an increased turnover, while standard medications try to reduce the bone turnover. A simulated therapy of a high-turnover osteoporosis with turnover-reducing drugs showed that transiently the mineral content displays an extraordinary homogeneity (**Fig. 2**). The long-term aim is to

design patient-specific therapies which bring an abnormal BMDD back to its original healthy state.

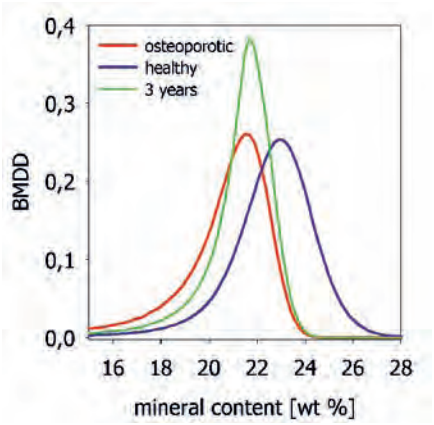


Fig. 2: The frequency distribution of the mineral content in bone (BMDD) and its time evolution during an antiresorptive therapy. Starting from a BMDD of increased turnover (red) and reducing the turnover to normal levels, brings the BMDD in the long term back to its healthy distribution (blue). Transiently (3 years after the start of the therapy) the BMDD displays a sharp peak (green).

Catanionic Bilayers

Catanionic systems are mixtures of amphiphilic molecules with oppositely charged headgroups. Arranged in bilayer structures the electrostatic forces result in an increase of the lateral cohesion energy. Peculiar mechanical behavior was observed experimentally, for example the formation of faceted hollow polyhedrons **[5]** and the extreme sensitivity of the phase diagram with respect to the molar ratio between anionic and cationic surfactants. Using computer simulations we explored the mechanical properties of a model membrane.

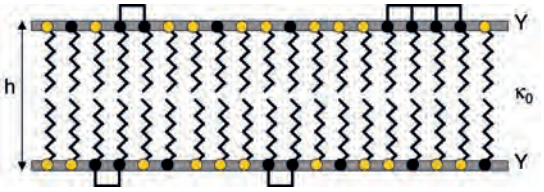


Fig. 3: Cross-section through a lipid bilayer membrane with negatively (black) and positively (yellow) charged headgroups. The schematic black bars connecting two neighboring anionic molecules indicate the formation of additional bonds (e.g., hydrogen bonds). The two charged bilayers are separated by an apolar core of low bending rigidity κ_0.

On a mesoscopic scale the model membrane consists of an apolar core and an upper and lower charged layer formed by the headgroups of the molecules (**Fig. 3**). In the microscopic description of the charged layer the headgroups occupy a triangular lattice. Two types of interaction are considered: the electrostatic interaction between headgroups and the hydrogen bonds between neighboring anionic headgroups modeled by harmonic springs. Membranes with a varying composition of anionic and cationic molecules have been first thermodynamically equilibrated and then mechanically tested. In agreement with experimental observations the simulation showed for high anionic concentrations extremely large bending rigidities of $\kappa > 500\ k_BT$ (**Fig. 4**). This stiffening of the membrane results from a rigidity percolation, i.e., the formation of a rigid backbone of hydrogen bonds in the charged layer. The mesoscopic sandwich-like structure of the membrane amplifies this effect since the apolar core separating the charged layers acts via a kind of lever-arm principle. Striking is also the narrowness of the region of concentrations in which the transition between soft and stiff bilayers occurs. In the case of electrostatic ordering between the molecules, the stiffening transition is postponed to higher concentrations of anionic headgroups further sharpening the soft-to-stiff transition.

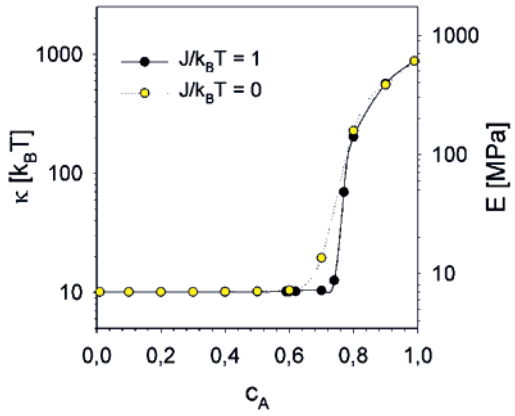


Fig. 4: Bending stiffness κ and effective elastic modulus E of the model membrane as a function of its composition (c_A denotes the concentration of negatively charged headgroups) for two different temperatures: yellow points correspond to a random arrangement of molecules, while black points include the effect of electrostatic ordering of the molecules. Note the semilogarithmic scale.

Polyelectrolyte Capsules

In collaboration with the Department of Interfaces we analyzed the deformation data of polyelectrolyte micro-capsules of well-defined geometry obtained with the atomic force microscope. In the limit of small deformations analytical results of shell theory can be applied, which were complemented by finite element calculations, giving quantitative information about the elastic modulus of the capsule wall material **[7]**. Variations of temperature and salt concentration lead to changes in the mechanical properties of the wall material and to changes in the capsule diameter **[8,9]**. The swelling-to-shrinking transitions were explained by an interplay of an expanding electrostatic force and a contracting surface tension **[9]**.

R. Weinkamer, J. Dunlop, P. Fratzl, M. Hartmann,
D. Ruffoni, P. Saparin
richard.weinkamer@mpikg.mpg.de

References:

[1] Weinkamer, R., Hartmann, M.A., Brechet, Y. and Fratzl, P.: Stochastic lattice model for bone remodeling and aging. Phys. Rev. Lett. **93**, 228102 (2004).

[2] Weinkamer, R., Hartmann, M.A., Brechet, Y. and Fratzl, P.: Architectural changes of trabecular bone caused by the remodeling process. Mater. Res. Soc. Symp. Proc. **874**, L.1.9.1 (2005).

[3] Hartmann, M.A.: Lattice models in Materials Science. PhD-Thesis, Humboldt University (2006).

[4] Ruffoni, D., Fratzl, P., Roschger P., Klaushofer, K. and Weinkamer, R.: The bone mineralization density distribution as a fingerprint of the mineralization process. Bone **40**, 1308-1319 (2007).

[5] Delorme, N., Dubois, M., Garnier, S., Laschewsky, A., Weinkamer, R., Zemb, T. and Fery., A.: Surface immobilization and mechanical properties of catanionic hollow faceted polyhedrons. J. Phys. Chem. B **110**, 1752-1758 (2006).

[6] Hartmann, M.A., Weinkamer, R., Zemb, T., Fischer, F.D., and Fratzl, P.: Switching mechanics with chemistry: A model for the bending stiffness of amphiphilic bilayers with interacting headgroups in crystalline order, Phys. Rev. Lett. **97**,018106 (2006).

[7] Elsner, N., Dubreuil, F., Weinkamer, R., Fischer, F.D., Fery, A.: Mechanical properties of freestanding polyelectrolyte capsules: a quantitative approach based on shell theory. Progr. Colloid Polym. Sci. **132**, 117-123 (2006).

[8] Mueller, R., Köhler, K., Weinkamer, R., Sukhorukov, G., Fery, A.: Melting of PDADMAC/PSS capsules investigated with AFM force spectroscopy. Macromolecules **38**, 9766-9771 (2005).

[9] Köhler, K., Biesheuvel, P.M., Weinkamer, R., Möhwald, H., and Sukhorukov, G.B.: Salt-Induced swelling-to-shrinking transition in polyelectrolyte multilayer capsules. Phys. Rev. Lett. **97**, 188301 (2006).

Biological and Bio-Inspired Materials

This section reviews some of the work on biological and bio-inspired materials conducted outside the research groups either with external partners or by postdoctoral researchers working independently (B. Aichmayer, R. Elbaum and P. Zaslansky).

Barbara Aichmayer 28.11.1975
2001: Diploma, Materials Science (University of Leoben, Austria)
Thesis: Further Development of a Nickel-Free Austenitic Steel
2005: PhD, Materials Science (Department of Material Physics, University of Leoben)
Thesis: Biological and Biomimetic Formation of Inorganic Nanoparticles
Since 2005: Postdoctoral scientist (Max Planck Institute of Colloids and Interfaces, Potsdam)

Rivka Elbaum 18.01.1971
1998: M. Sc. degree, Chemistry (The Weizmann Institute of Science, Israel)
Thesis: Synthesis and surface characterization of CdS and CdSxSe1-x nanocrystals
2005: PhD, Chemistry (The Weizmann Institute of Science, Israel)
Thesis: Preservation and evolution of ancient DNA of plants in the Levant: study in phytoliths and olive pits
2005: Postdoc, Chemistry (The Weizmann Institute of Science, Israel)
Topic: The 3D structure of cattle incisors
2006: Humboldt Postdoctoral Fellow, Biomaterials (Max Planck Institute for Colloids and Interfaces) Topic: The mechanical role of silica in wheat

Paul Zaslansky 16.10.1967
1985-1991 Doctor of Medical Dentistry (Hebrew University of Jerusalem)
1991-2000 Clinical Dentistry in public and private clinics
2000-2005 PhD, Chemistry (Weizmann Institute of Science, Rehovot)
Thesis: Human Tooth Structure-Function Relations: a Study of Mechanisms of Stress Distribution During Mastication
Since 2005: Postdoctoral Scientist: (Max Planck Institute of Colloids and Interfaces, Potsdam)

Structure and Properties of Glass Sponges

The structure and the mechanical design of different glass sponges are investigated in collaboration with colleagues from Bell Labs (Joanna Aizenberg and Co-workers), UCSB (James Weaver and Dan Morse), among others. A major result is the description of the hierarchical structure of the glass sponge Euplectella **[1]**, consisting of glass spicules joined by a silica matrix (**Fig.1**). The spicules consist of laminated glass with a succession of micron-sized silica layers and nanometer-sized protein layers and possess remarkable mechanical properties **[2]**.

*Fig. 1: skeleton of the glass sponge Euplectella **[1]***

Mechanics and Thermodynamics of New Materials

A further collaboration with Bell Labs (J. Aizenberg and co-workers) is the development and mechanical description of new types of active materials based on hydrogels stabilized by silicon posts which may be free-standing or attached to a surface (**Fig. 2**). The silicon posts bend reversibly upon drying of the gel, leading to the formation of complex micro-patterns and to micro-actuation **[3]**.

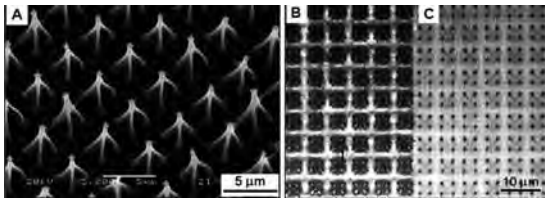


*Fig. 2: Groups of four silicon posts join up by drying of the gel between them (A). This generates **[3]** a complex micro-pattern (B), which can be reversed upon rehydration (C)*

Further research with the University Leoben includes, for example, the theoretical description of unstable and moving interfaces in materials **[4]**, or the fracture mechanisms in certain polymers at the micro- and nanoscale **[5]**.

Bio-Inspired Polymer-Mineral Composites (Barbara Aichmayer)

In biomineralization, the nucleation and growth of inorganic crystals are controlled by biological macromolecules. For instance, amelogenin proteins play a key role in the formation of tooth enamel. In cooperation with H. Margolis *et al.* (Forsyth Institute, Boston) and R. Sigel (Colloid Dept.) we studied the self-assembly of different amelogenins in solution **[6]**. It was shown that amelogenins form so-called "nanospheres", which can further aggregate into assemblies of multiple nanospheres (see **Fig. 3**).

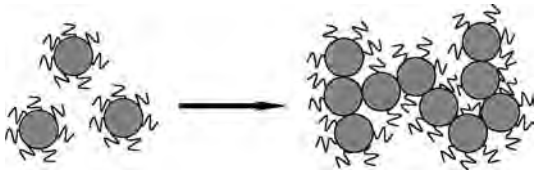


Fig. 3: Model for the aggregation of amelogenin nanospheres at pH 8.

Further studies showed that the shape of the individual building blocks can better be described by an ellipsoidal (or even disc-like) shape and that the aggregation depends more strongly on the pH value than on the temperature. In the presence of growing elongated hydroxyapatite crystals, the aggregates sketched in **Fig. 3** might be modified towards a higher degree of ordering, which would imply a parallel alignment of the mineral crystals, as typical for the structure of enamel. In order to elucidate, how the protein assemblies guide the crystal growth in enamel formation, our current and future research activities focus on in vitro mineralization studies.

Biomineralization can be mimicked by using artificial polymers to manipulate crystal growth. In cooperation with H. Cölfen *et al.* (Colloid Dept.), we investigate the biomimetic formation of calcite crystals in the presence of polystyrene sulfonate (PSS) **[7]**. Scattering measurements of single mineral particles, using a µ-focus beam (at BESSY, Berlin and ESRF, Grenoble) were performed to study the influence of PSS on the structure of µm-sized calcite particles. First results show that the polymeric additive led to a transition from single crystals to strongly textured polycrystals with structural features below 10nm.

Finally, the nucleation and growth of metal nanoparticles on bacterial S-layers were investigated quantitatively by small-angle x-ray scattering **[8]**.

The general scope of these structural studies is to contribute to a better understanding of biological and biomimetic mineralization.

The Materials Design of Wheat Awns for Seed Dispersal (Rivka Elbaum)

Awns evolved to direct seeds to a safe germination position. The dispersal unit of wild wheat (Triticum diccocoides) bears two pronounced awns that balance the seed as it falls to the ground **[9]**.

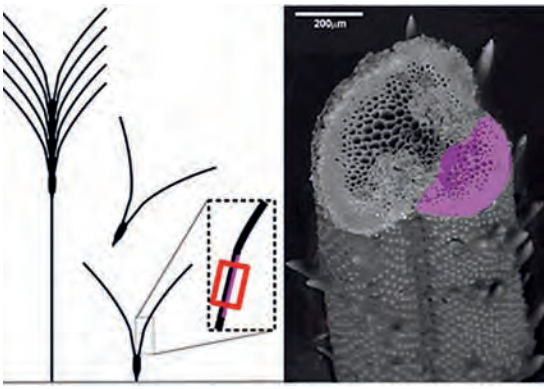


Fig. 4: A graphic illustration of the wild wheat plant and two dispersal units (not in scale), are shown on the left. Each dispersal unit carries two pronounced awns that orient the dispersal unit as it falls. The red square indicates the location of the scanning electron micrograph on the right, and the active cellulose zone is indicated in pink.

Using X-ray diffraction we found that the cellulose fibrils, which construct the cell walls, are aligned mostly along the long axis of the awn, except at a region close to the seeds (highlighted in **Fig. 4**). In this location the fibers are randomly oriented. This design results in bending of the awns with changes of humidity: water molecules that adsorb to the fibers cause mostly a lateral expansion. Thus, the whole structure will expand laterally except for the region where the fibrils are randomly oriented. This part of the awn will expand in all directions, pushing the awns toward each other. With drying, this active region will contract, similarly to a muscle.

Fig. 5: Wild wheat awns at different levels of relative air humidity (r.h.)

Cycling the air humidity causes a periodic movement of the awns, resembling the swimming motion of frog legs. **Fig. 5** shows this principle of the dispersal unit movement. It is clearly visible that the average distance between the awns changes as a function of air humidity. With the daily humidity cycle, the awns will move cyclically and thereby propel the dispersal unit forward. Silicified hairs that cover the awns and point away from the seed are locking the awn in this process and preventing a backward movement. This suggests the possibility that the daily humidity cycle may induce the motility required for seed dispersal. This also means that a dead plant tissue can work as a motor fuelled just by the ambient humidity cycle **[10]**.

Structure-Function Relations of Human Teeth in 3D (Paul Zaslansky)

Teeth are composed of mainly two carbonated hydroxyapatite based composite materials (enamel and dentin), arranged in a complex array of graded and varying micro structures. Systematic structural variations of tooth materials **[11]** lead to very different responses to load within different parts of the crown and root. Consequently, the function of whole teeth and the nature of differences between different types of teeth are not well understood. Our work focuses on trying to better understand design principles of human teeth by combining 2D imaging techniques (wet-mode environmental scanning electron microscopy, X-ray scattering techniques and Acoustic and Raman microscopy) of static and mechanically loaded tooth samples with 3D high resolution (sub µ) measurements (using microtomography and speckle interferometry). Our working premise is that there is great importance to both arrangement and properties of features embedded in the microstructure **[11,12]** and both are needed to support the longevity of teeth. By matching structural and deformation patterns from 2D slices with non-destructive measurements of the 3D samples, we hope to understand what allows teeth to function without remodeling or 'self-repair' the way that bones do.

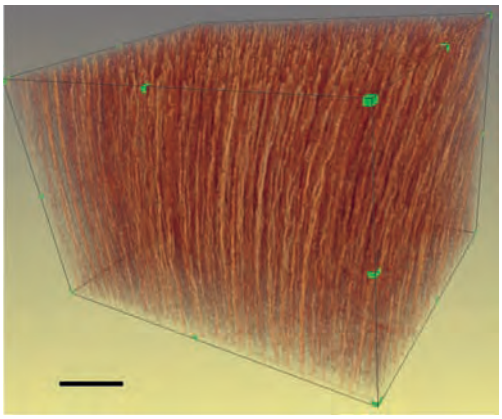


Fig. 6: 3D virtual cube of dentin displaying tubules running upward through the structure. The phase enhanced image, obtained at ID19 in the ESRF clearly shows the distribution, density and orientations of the highly mineralized tubules. Scale bar: 100 µm

Much of our 3D characterization is based on imaging of interference patterns and as a result we obtain spatial sub-micron resolution using currently available partially-coherent laser and X-ray sources **[12]**. As seen in **Fig 6**, our methods produce data with a resolution capable of resolving ~1 micrometer thick tubules in dentin (or similarly prisms in enamel). We are thus able to track displacements and image the microstructure, and our efforts are aimed at correlating the deformation patterns so as to understand the behavior of human teeth under physiological (daily) mechanical load.

B. Aichmayer *Barbara.Aichmayer@mpikg.mpg.de*
R. Elbaum *Rivka.Elbaum@mpikg.mpg.de*
P. Zaslansky *Paul.Zaslansky@mpikg.mpg.de*
P. Fratzl *Peter.Fratzl@mpikg.mpg.de*

References:

[1] J. Aizenberg, J.C. Weaver, M.S. Thanawala, V.C. Sundar, D.E. Morse, P. Fratzl: Skeleton of Euplectella Sp.; structural hierarchy from the nanoscale to the macroscale. Science **309**, 275 - 278 (2005).
[2] A. Woesz, J.C. Weaver, M. Kazanci, Y. Dauphin, J. Aizenberg, D. E. Morse, P. Fratzl: Micromechanical properties of biological silica in skeltons of deep-sea sponges. J. Mater. Res. **21**, 2068 -2078 (2006).
[3] A. Sidorenko, T. Krupenkin, A. Taylor, P. Fratzl, J. Aizenberg: Reversible switching of hydrogel-actuated nanostructures into complex micropatterns. Science **315**, 487-490 (2007).
[4] P. Fratzl, F.D. Fischer, J. Svoboda: Energy dissipation and stability of propagating surfaces. Phys. Rev. Lett. **95**, 195702 (2005).
[5] G.A. Maier, G. Wallner, R.W. Lang, P. Fratzl: Structural changes during plastic deformation at crack Tips in PVDF films. Macromol. **38**, 6099 - 6105 (2005).
[6] Aichmayer, B., Margolis, H.C., Sigel, R., Yamakoshi, Y., Simmer, J.P. and Fratzl, P.: The onset of amelogenin nanosphere aggregation studied by small-angle X-ray scattering and dynamic light scattering. J. Struct. Biol. **151**, 239-249 (2005).
[7] Wang, T., Antonietti, M. and Cölfen, H.: Calcite Mesocrystals: "Morphing" Crystals by a Polyelectrolyte. Chem. Eur. J. **12**, 5722-5730 (2006).
[8] B. Aichmayer, M. Mertig, A. Kirchner, O. Paris, P. Fratzl: Small-angle scattering of S-layer mineralization. Adv. Mater. **18**, 915-919 (2006).
[9] Chambers, J. C., MacMahon, J. A: A Day in the Life of a seed: Movements and fates of seeds and their implications for natural and managed system Annu. Rev. Ecol. Syst. **25**, 263-292 (1994).
[10] R. Elbaum, L. Zaltzman, I. Burgert, P. Fratzl: The role of wheat awns in the sead dispersal unit, Science **316**, 884-886 (2007).
[11] P. Zaslansky, A. A. Friesem and S. Weiner: "Structure and mechanical properties of the soft zone separating bulk dentin and enamel in crowns of human teeth: Insight into tooth function", J. Struct. Biol. **153** (2), 188-199 (2006).
[12] S. Zabler, H. Riesemeier, P. Fratzl and P. Zaslansky: "Fresnel-propagated imaging for the study of human tooth dentin by partially coherent x-ray tomography", Opt. Express **14** (19), 8584-8597 (2006).

Mesoscale Materials and Synchrotron Research

Oskar Paris 26.01.1967
1993: Diploma, Physics
(University of Vienna, Austria)
Thesis: Internal Oxidation of
Cu-Fe Alloys
1996: PhD, Physics
(University of Vienna, Austria)
Thesis: Influence of Internal and
External Stresses on Decomposition
in Alloys
1996-1998: Postdoc
(Federal Institute of Technology,
Institute of Applied Physics,
Zurich, Switzerland)
1998-2003: University Assistant
(University of Leoben, Austria)
2003: Habilitation,
(University of Leoben, Austria)
Thesis: Structure and Properties
of Complex Materials: Synchrotron
Radiation and Neutrons as Local Probes
Since 2003: Group Leader
(Max Planck Institute of Colloids
and Interfaces, Potsdam)

Mesoscale materials exhibit particular structural features at intermediate scales between the atomic/molecular world and macroscopic dimensions. Such systems may show novel properties and functions which result directly from the size of the compartments and/or the interactions between the individual structural units. Our research is directed towards the structural characterization and the understanding of structure-function relationships of hierarchical mesoscale composites such as biological materials, and (biomimetic) carbons and ceramics. Moreover, we are interested in the phase behavior of fluids in confined geometry of mesopores, and in their elastic interaction with the solid pore walls. Our experimental approaches are essentially based on scattering techniques using synchrotron radiation. We develop sophisticated new *in-situ* methods to "watch materials at work", and we apply microbeam scanning techniques to map the local nanostructure in hierarchically organized materials.

Biomimetic Processing

The aim here is to transform hierarchical plant tissues into inorganic materials, and to characterize their structure and transformation behavior. In a first approach, infiltration of wood with ceria nanoparticles in a suitable acidic solution was successfully used to replace the lignin phase with the nanoparticles (nano-casting). Upon subsequent calcination, macroscopic ceramic replicas that reproduce four distinct hierarchical levels of the original biological wood template were obtained **[1]**. In particular, it was shown for the first time with the aid of small-angle X-ray scattering (SAXS) that the spiraling cellulose microfibrils in wood could be cast with nanometer precision (**Fig. 1**). This opens new possibilities for the simple and economical synthesis of novel ceramics with hierarchical and directional porosity.

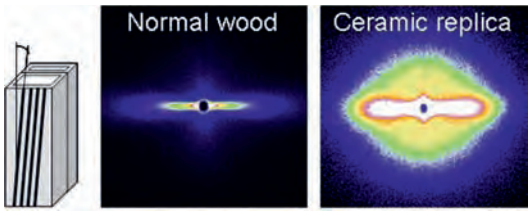


Fig. 1: SAXS patterns illustrating that the microfibrillar cellulose orientation is fully reproduced after nanoparticle casting of wood.

The second approach used direct conversion of tissues by pyrolytic decomposition of the plant biopolymers. We have studied the structural and chemical development of pyrolysed wood as a function of temperature up to 2400°C. We could show that crack free carbon monoliths which fully resemble the honeycomb-like cellular architecture of wood tissue, could be produced with a preferred carbon orientation along the cell axis **[2]**. The thermal decomposition of wood cellulose was further investigated with *in-situ* X-ray diffraction. By quantitatively analyzing the kinetics for different temperatures it was found that decomposition of the crystalline cellulose in wood occurred mainly via a thermally activated decrease of the microfibril diameter.

As a second model system for direct biomimetic conversion of plants, we have investigated the silica accumulating stalks of *Equisetum hyemale* (horsetail or scouring rush). Besides a general interest in the function of silica in higher plants, we used horsetail for direct SiC synthesis by controlled pyrolysis taking the biopolymers as a carbon source and silica as a Si- source. Ongoing work is focusing on the detailed characterization of the type and distribution of silica, and on the optimization of the conversion process in terms of yield and type of SiC.

Mesoscale Carbons

The detailed origin of the extraordinary mechanical properties of carbon fibers and the relation to their local mesoscale structure are still largely unknown. In a pioneering experiment in cooperation with the University of Vienna we combined *in-situ* bending of single carbon fibers with high resolution X-ray diffraction by scanning the bent fibers across a 0.1 µm wide beam (**Fig. 2**). Strain redistribution across the fiber with a shift of the neutral axis allowed a quantitative determination of the elastic moduli in compression and in tension. A significant change of the preferred carbon orientation in the compression regime proved that buckling of the carbon nanocrystallites is the physical origin of the difference in tensile and compressive properties. Differences between different carbon fiber types were attributed to different amounts of covalent cross-links connecting the crystallites **[3]**.

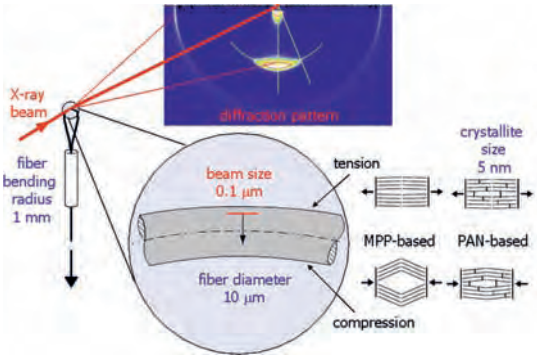


Fig. 2: Sketch of the in-situ bending experiment to determine the local mechanical properties of carbon fibers.

Further work on mesoscale carbons included the local mechanical properties of pyrolysed wood at the level of single cell walls using nanoindentation **[4]**, and a critical examination of the classical way to obtain carbon crystallite sizes from Raman band intensity ratios **[5]**. One of the future challenges of our research in this field is related to the important role of covalent cross-links for the mechanical behavior in disordered carbons. In this respect, we have already started *in-situ* high temperature creep studies of single carbon fibers within the synchrotron radiation X-ray microbeam at the µ-Spot beamline at BESSY.

Fluids in Mesopores

Mesoporous materials with narrow distributions of pores on highly ordered lattices are ideal model systems to study the phase behavior of fluids in confinement. In cooperation with the Technical University of Berlin, we have developed a sorption device for *in-situ* small-angle X-ray diffraction. Sorption of organic fluids in 2D hexagonal lattices of SBA-15 silica materials was investigated at Hamburger Synchrotronstrahlungslabor (HASYLAB), and more recently at the µ-Spot beamline at BESSY. Analyzing the intensity of the diffraction peaks as a function of vapor pressure along a sorption isotherm provides detailed structural information on liquid film formation and on pore condensation **[6]**. Moreover, high capillary pressures lead to a deformation of the pore walls at capillary condensation. The adsorption strains related to the deformation of the pore lattice can directly be obtained from the shift of the diffraction peaks as a function of vapor pressure (**Fig. 3**) **[7]**.

In the future, we propose to investigate the dynamic interaction between pore deformation as a consequence of capillary condensation, and the influence of these deformations on the phase behavior of the fluid. Moreover, we plan to develop a mechanical model that quantitatively explains the experimentally observed behavior. This activity is embedded in the framework of the Collaborative Research Center Sfb 448 "Mesoscopically Organized Composites" of the German Research Foundation (DFG).

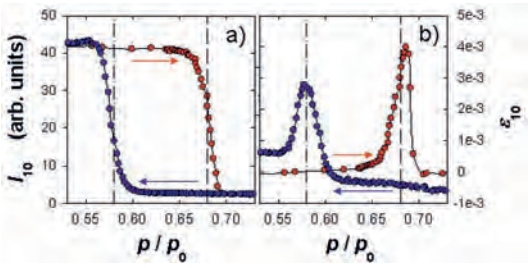


Fig. 3: In-situ sorption of perfluoropentane (C_5F_{12}) in SBA-15 (red: adsorption; blue: desorption). a) shows the integrated intensity of the 10 reflection which is low for entirely filled pores due to partial contrast matching, and b) shows the corresponding lattice strains.

From Diffraction to Imaging

A large part of our activities in the field of synchrotron research in the last two years were related to the commissioning of an experimental station for simultaneous microbeam small- and wide-angle scattering (SAXS/WAXS) at the microfocus (µ-Spot) beamline at BESSY in Berlin. The instrument is now fully operational and provides a routine microbeam of 10 µm diameter at a flux of more than 10^9 *photons per second* **[8]**. A series of user experiments have already been performed in cooperation with other research groups from the department and with external partners. Many of them were related to scanning SAXS/WAXS studies on biological or bio-inspired materials such as for instance bone, plant tissues, and biomimetic calcite.

A long-term goal of our research is to proceed from microbeam scanning SAXS/WAXS to a real imaging technique. There has been considerable progress in our group concerning software development for interactive instrument control combined with online data analysis and online parameter imaging. This work was done in close collaboration with the European Synchrotron Radiation Facility (ESRF) in the framework of a long-term proposal. At present, several software tools are available that allow an automated extraction and imaging of nanostructural parameters such as local fiber orientation from WAXS (**Fig. 4**) or particle size and orientation from SAXS. Future work is directed towards the implementation of these tools into the beamline software at BESSY.

Furthermore, we plan to extend our scanning approach to the third dimension in both, the reciprocal space (local texture analysis) and in real space (SAXS tomography, confocal diffraction).

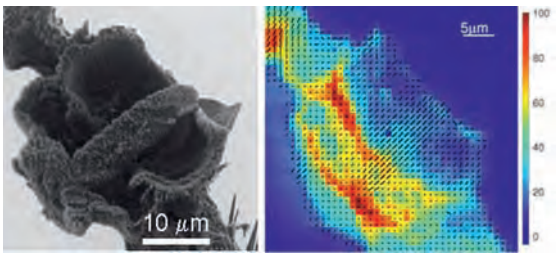


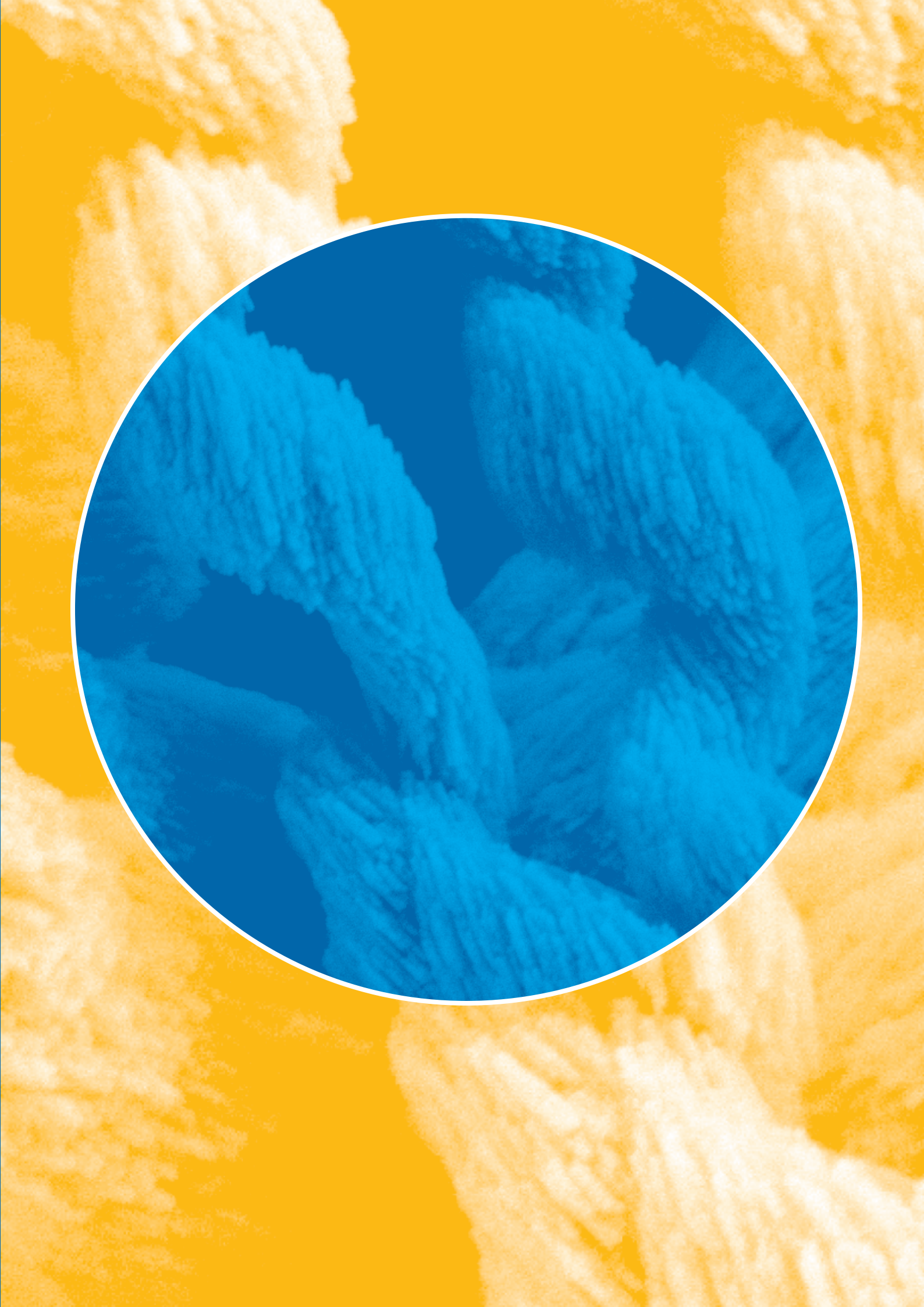
Fig. 4: SEM image (left) and an image based on scanning microbeam diffraction (right) of a flow sensing system in cricket appendices. The color scale on the right is given by the intensity of the equatorial 040 reflection from the crystalline chitin fibers in this chitin/protein nanocomposite, and the bars indicate the local chitin fiber orientation as deduced from the individual diffraction patterns. The sample was prepared by using a UV microlaser instrument and the diffraction experiments were performed at the ESRF [9].

O. Paris, A. Deshpande, A. Gourrier, C. Li, L. Sapei, R. Seidel, S. Siegel, G. Weseloh, I. Zenke, G. A. Zickler
oskar.paris@mpikg.mpg.de

References:

[1] Deshpande, A., Burgert, I. and Paris O.: Hierarchically structured ceramics by high-precision nanoparticle casting of wood. Small **2**, 994-998 (2006).
[2] Paris, O., Zollfrank C. and Zickler G.A.: Decomposition and carbonization of wood biopolymers – A microstructural study of softwood pyrolysis. Carbon **43**, 53-66 (2005).
[3] Loidl, D., Paris, O., Burghammer, M., Riekel, C. and Peterlik, H.: Direct observation of nanocrystallite buckling in carbon fibers. Phys. Rev. Lett. **95**, 225501 (2005).
[4] Zickler, G., Schöberl, T and Paris, O.: Mechanical properties of pyrolysed wood: A nanoindentation study. Phil. Mag. A. **86**, 1373-1386 (2006).
[5] Zickler, G., Gierlinger, N., Smarsly, B., Peterlik, H. and Paris O.: A reconsideration of the relationship between the crystallite size La of carbons determined by X-ray diffraction and Raman spectroscopy. Carbon **44**, 3239-3246 (2006).
[6] Zickler, G., Jähnert, S., Wagermeier, W., Funari, S., Findenegg, G. and Paris, O.: Physisorbed films in periodic mesoporous silica studied by *in-situ* synchrotron radiation small-angle diffraction. Phys. Rev. B **73**, 184109 (2006).
[7] Zickler, G.A., Jähnert, S., Funari, S., Findenegg, G. and Paris, O.: Pore lattice deformation in ordered mesoporous silica studied by in-situ small-angle X-ray diffraction. J. Appl. Cryst. **40**, 522-526 (2007).
[8] Paris, O., Li, C., Siegel, S., Weseloh, G., Emmerling, F., Riesemeier, H., Erko, A. and Fratzl, P.: A new experimental station for simultaneous microbeam scanning small-and wide-angle scattering at BESSY. J. Appl. Cryst. **40**, 466-470 (2007).
[9] Seidel R., Gourrier A., Burghammer M., Riekel C., Geronimidis G. and Paris O.: Mapping fibre orientation in complex-shaped biological systems with micrometre resolution by scanning X-ray microdiffraction, Micron (2007) in press (doi:10.1016/j.micron.2007.02.004).

COLLOID CHEMISTRY

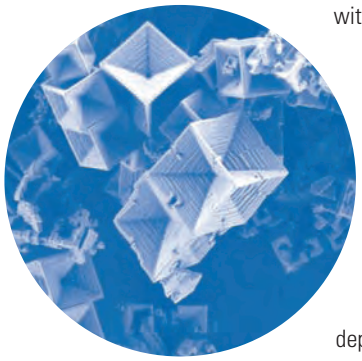


Research in the Department of Colloid Chemistry

Scientific Profile

The activities of the Colloid Chemistry Department are a mixture of long-standing strongholds which partly can be traced back to the institute's predecessors, activities stimulated by the director, and new topics independently developed by young researchers. The overall size of the department is 60 people, covering a wide range of research topics.

The effective constituting element of the department are "research groups" or "projects", a functional research structure headed by a senior scientist and which involves 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 redefine 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 with the institute.



Incentives for the choice of a new research direction are usually scientific curiosity and promise, but research is sometimes 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 continuously come from the outside.

In detail, the following topics are found in 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 a better understanding of the nucleation process and particle formation. For this purpose, new experimental online multidetection techniques are developed and supplemented by theoretical approaches *(Dr. Klaus Tauer)*. Other projects strive for the synthesis of complex polymer molecules (e.g. block & graft copolymers) and colloids (e.g. core-shell latexes, reinforced materials) by emulsion polymerization and a rational chemical use of the particle interfaces *(Dr. Klaus Tauer)*.

Self-Organizing Polymers

Amphiphilic polymers consist of components which 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 also unusual dispersion problems can be solved. Focal points of interest in this range are:

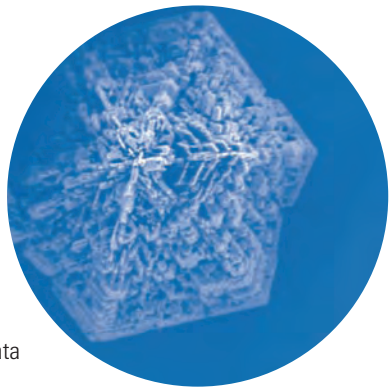
- The micelle formation and lyotropic liquid crystalline phase behavior of amphiphilic polymers is examined in dependence of molecular parameters as well as the amount of solubilized material *(Dr. Helmut Schlaad)*. For that, novel side chain functional copolymers are prepared, e.g. some with sugar moieties.

- 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. Hans Börner)*.

- 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 co-polymers 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 world of synthetic polymers. We also expect that such polymers help to address the interface between the biological and technical systems, such as in implants or microstructured diagnostic systems *(Dr. Hans Börner)*.



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

- The synthesis of new well defined nanoparticles with function by solvent and ligand assisted synthetic nonaqueous solgel pathways and their self-assembly into organized 3D superstructures by ligand encoding *(Dr. Markus Niederberger). This activity has left the institute effective to the 1.1.2007 with the promotion of Dr. Niederberger to the rank of a Professor at the ETH Zürich.*

- The synthesis of mesoporous polymers and carbonaceous materials for catalysis and energy applications *(Dr. Arne Thomas).* This work is part of the Max Planck project house "ENERCHEM" (a cooperation of 5 institutes) and is devoted to design new supports, electrode materials and porous systems for energy storage. Highlights in this area are novel fuel cell membrane polymers and the development of a new set of metal free catalysts based on carbon nitrides.

- The synthesis of mesoporous carbon structures by hydrothermal techniques for the sake of Advanced Chromatography and nanoparticles encapsulation *(Dr. Maria Magdalena Titirici).*

- 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 *(Prof. Markus Antonietti).*

- The generation of crystalline thin mesoporous layers by evaporation induced self-assembly (EISA) for electrochemistry and sensing *(Dr. Bernd Smarsly) This activity will effectively leave the institute to the 1.7.2007 with the promotion of Dr. Smarsly to the rank of a Professor at the University of Gießen.*

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 scientific 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 and enantiomer-selective crystallization *(Dr. Helmut Cölfen).*

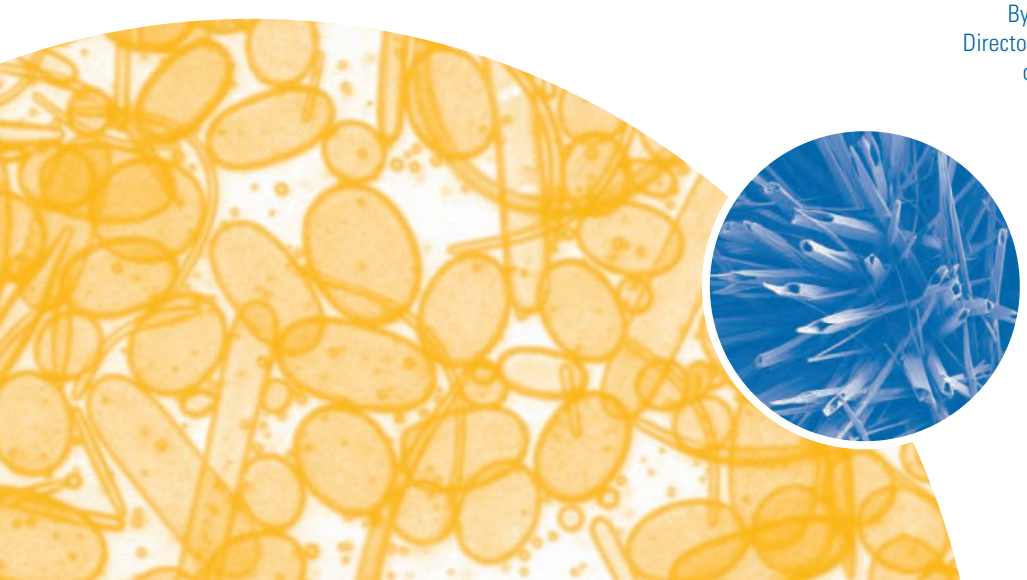
- Special techniques of transmission and scanning electron microscopy on soft, structured matter *(Dr. Jürgen Hartmann).*

- Development of new techniques of dynamic light scattering to colloidal systems, e.g. using optical near fields or a newly developed ellipsometric light scattering technique. *(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 ultra-centrifugation, 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.

By Markus Antonietti,
Director of the Department
of Colloid Chemistry



Polymer Dispersions/Heterophase Polymerizations

Modern developments of polymer chemistry are waiting to be applied to industrially important aqueous heterophase polymerization techniques. Research topics over the last two years were basic investigations regarding the application of new radical polymerization techniques and tools under heterophase conditions and the continuation of our studies on particle nucleation in emulsion polymerization.

Klaus Tauer 27.09.1951
1974: Diploma, Polymer Chemistry (Friedrich Schiller University, Jena)
Thesis: Dye Sensitization of Photoconductivity of Poly(arylene 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)
Since 2004: "Privatdozent" Polymer Colloids, University of Potsdam

Controlled Radical Polymerization

Dithioesters can be used as reversible addition fragmentation transfer agents (RAFT agents) in batch ab-initio emulsion polymerization to control the polymer growth. The outcome of the polymerization is strongly influenced by the water solubility of both the RAFT agent and the initiator. The highest control inside the latex particles is achieved and the lowest amount of coagulum is formed if a completely water soluble initiator such as potassium peroxodisulfate is employed in combination with moderately water soluble RAFT agents such as benzyl dithioacetate. Compared to the RAFT-free experiment the rate of polymerization is slightly reduced (but complete conversion is achieved in any case), the average molecular weight is reduced, and the molecular weight distribution is considerably narrowed **[1]**. The crucial step is the sorption of the RAFT agents by the latex particles. The experimentally determined sorption order of the RAFT agents matches very well with the order of the average molecular weights of the polymer inside the latex particles that is the lower the higher the water solubility of the RAFT agent **[2, 3]**.

Control of radical heterophase polymerizations regarding the formation of block copolymer particles is easily possible by seeded polymerization techniques with seed particles functionalized either by RAFT agents or by 1,1-diphenylethylene **[4]**. The second stage polymerization of the swollen seed particles in the absence of a free monomer phase is an almost perfect realization of the nano-reactor concept. Structured latex particles with average diameters below 50 nm and various morphological features such as core / shell or acorn-like morphologies are accessible (cf. **Fig. 1**). The block copolymer yield is in all cases larger than 70 % (in most cases above 90 %).

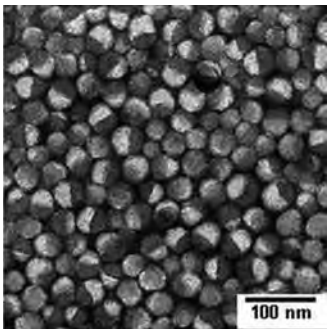


Fig. 1: TEM images of PS(DPE)-b-PtBMA nanoparticles prepared with potassium peroxodisulfate as initiator during the second stage polymerization; multiple staining with phosphor tungstic acid (PTA) and RuO_4; darker regions are polystyrene (PS) domains and lighter regions are poly(tert.-butyl methactylate) (PtBMA) domains.

During these studies two experimental observations of general importance for heterophase polymerizations have been made. First, also hydrophilic radicals stemming from the initiator enter the latex particles **[5]** and second, latex particles can be modified by sorption even of extremely hydrophobic solids if applied as solution in non-water-miscible solvents (cf. **Fig. 2**) **[6]**.

Fig. 2: Images of the original 35 nm PS latex (left) and tinted with the hydrophobic dyes Sudan IV (middle) and Solvent Blue (right)

Microwaves as Heating Tool [7-9]

Aqueous radical heterophase polymerizations may be carried out in microwave ovens because the polar nature of the continuous phase allows for efficient microwave coupling. This dielectric heating is extremely fast as the reaction mixture can be warmed up within about 12 seconds from room temperature to > 90 °C. Comparable with radiation induced polymerization pulsed thermal polymerizations (PTP) with alternating 'hot' and 'cold' stages as illustrated in **Fig. 3** give rise to conditions, in which the cold stages are perfect post-effect situations leading to polymers with extremely high molecular weights (above 10^7 g/mol).

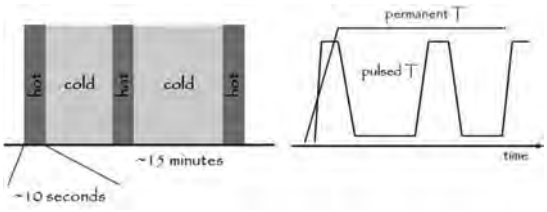


Fig. 3: Illustration of the pulsed thermal polymerization (PTP) procedure (left) with cycles of alternating hot and cold stages and the temperature profiles during polymerizations with pulsed and permanent heating (right)

Compared with 'normal' radical polymerizations PTP of aqueous miniemulsions are characterized by two peculiarities: (1) Medium hydrophobic initiators such as 2,2'-azobisisobutyronitrile (AIBN) and PEGA200 [poly(ethylene glycol)-azo-initiator] lead to largely enhanced conversion rates compared to the much more hydrophilic potassium peroxodisulfate or the much more hydrophobic 2,2'-azobis(2-methyl-butyronitrile) and (2) high polymerization rates and extremely high molecular weights can be realized simultaneously.

Particle Nucleation [9]

Thermodynamics requires in any heterophase system an exchange of matter between all phases. Thus, aqueous phase kinetics plays a crucial role even if hydrophobic initiators are employed. In order to study the role of aqueous phase reactions particle nucleation during the surfactant-free emulsion polymerization of styrene has been studied with AIBN as initiator. The initiator was injected either into the monomer phase (mode 1) or into the water phase (mode 2). Surprisingly, polymerization was observed in both phases. Besides the expected bulk polymer in the monomer phase also latex particles were obtained (cf. TEM images of **Fig. 4**).

Moreover, the reactions in the aqueous phase lead initially to a change in the conductivity and subsequently to the formation of latex particles accompanied by the drop in the transmission (**Fig. 5**). The shape of the conductivity curve is qualitatively the same as observed for surfactant-free emulsion polymerizations initiated with potassium peroxodisulfate. **[10, 11]**

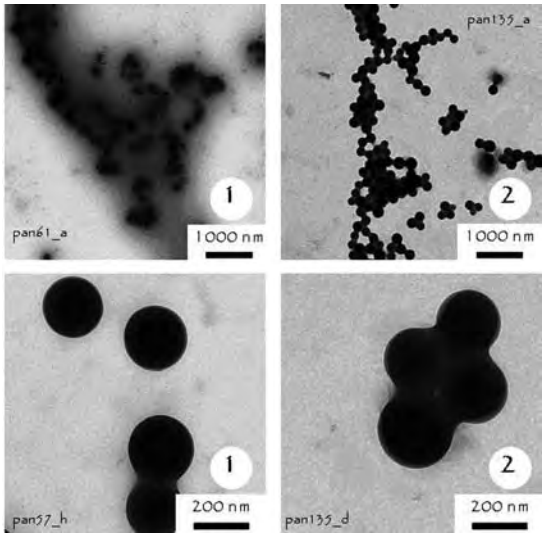


Fig. 4: TEM images of latex particles obtained during surfactant-free emulsion polymerization of styrene initiated with AIBN; 1,2 – AIBN injection modes

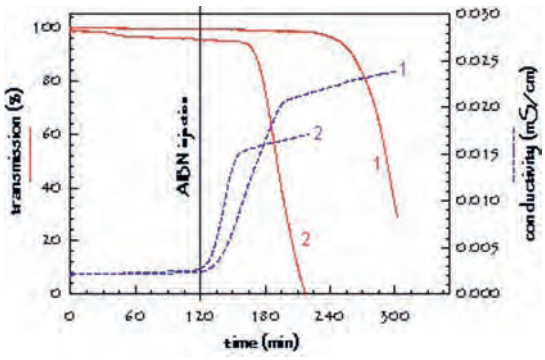


Fig. 5: On-line record of the changes in transmission (red lines) and conductivity (blue lines) during AIBN-initiated surfactant-free styrene heterophase polymerization, 70 °C; the curves represent averages of 5 repeats; 1, 2 AIBN addition into the monomer and the water phase, respectively

The bend of the conductivity curves marks the onset of particle nucleation as conducting species are captured in the diffuse electrical double layer of the particles. These results clearly prove that side reactions of carbon radicals in water lead to conducting species. The zeta-potential of the particles is pH-dependent and negative at pH > 4.

K. Tauer, A. M. I. Ali, M. Antonietti, C. Holtze, J. W. Lee, P. Nazaran, S. Nozari,
klaus.tauer@mpikg.mpg.de

References:

[1] Nozari, K., Tauer, K.: Calorimetric Study on the Influence of the Nature of the RAFT Agent and the Initiator in Ab Initio Aqueous Heterophase Polymerization. Polymer **46**, 1033-1043 (2005).
[2] Nozari, S., Tauer, K., Ali, A.M.I.: RAFT Agent Concentration in Polymer Particles during Emulsion Polymerization. Macromolecules **38**, 10449-10454 (2005).
[3] Nozari, S., Tauer, K.: Time-dependent Study of RAFT-mediated Ab-initio Batch Emulsion Polymerization of Styrene. Macromolecules, submitted
[4] Viala, S., Tauer, K., Antonietti, M., Lacik, I., Bremser, W.: Structural control in radical polymerization with 1,1-diphenylethylene. Part 3. Aqueous heterophase polymerization. Polymer **46**, 7843-7854 (2005).
[5] Tauer, K., Nozari, S., Ali, A.M.I.: Experimental reconsideration of radical entry into latex particles. Macromolecules **38**, 8611-8613 (2005).
[6] Tauer, K., Nozari, S., Ali, A.M.I., Kozempel, S.: Sorption of Hydrophobic Organic Compounds by Aqueous Latexes. Macromol. Rapid Commun. **26**, 1228–1232 (2005).
[7] Holtze, C., Antonietti, M., Tauer, K.: Ultra-fast Conversion and Molecular Weight Control through Temperature Programming in Microwave-Induced Miniemulsion Polymerization. Macromolecules **39**, 5720-5728 (2006).
[8] Holtze, C., Tauer, K.: Surviving Radicals – Promises of a Microwave-Effect on Miniemulsion-Polymerization for Technical Processes. (Invited paper) Macromol. Rapid Commun., in press
[9] Tauer, K: Mukhamedianjova, M., Holtze, C., Nazaran, P., Lee, J. W.: Unusual kinetics in aqueous heterophase polymerizations. Macromol. Symp., in press
[10] Kuehn, I., Tauer, K.: Macromolecules **28**, 8122-8128 (1995).
[11] Tauer, K., Padtberg, K., Dessy, C.: ACS Symp. Ser. **801**, 93-112 (2002).

Biohybrid Polymers

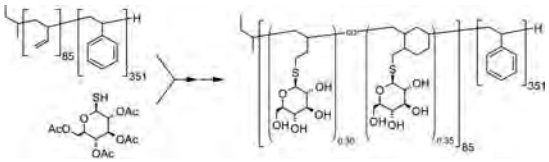
Helmut Schlaad 04.08.1967
1993: Diploma, Physical Chemistry (University of Mainz)
Thesis: Studies of the Anionic Polymerization of Methyl Methacrylate in Toluene in the Presence of Aluminium Alkyls
1997: PhD, Physical Chemistry (University of Mainz)
Thesis: Studies of the Mechanism of the Anionic Polymerization of Methacrylates in the Presence of Aluminium Alkyls in Toluene
1998: Postdoc (University of Massachusetts, Lowell, USA)
Since 1999: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2004: Senior Scientist (Max Planck Institute of Colloids and Interfaces, Potsdam)
2004: Habilitation, Physical Chemistry (University of Potsdam)
Thesis: Polymer Self-Assembly: Adding Complexity to Mesostructures of Diblock Copolymers by Specific Interactions

References:
[1] M. Groenewolt, T. Brezesinski, H. Schlaad, M. Antonietti, P. W. Groh, B. Ivan: Polyisobutylene-block-poly(ethylene oxide) for robust templating of highly ordered mesoporous materials. Adv. Mater., 1158-1162 (2005).
[2] R. M. Kandre, F. Kutzner, H. Schlaad, A. D. Schlüter: Synthesis of high molecular weight amphiphilic polyphenylenes by Suzuki polycondensation. Macromol. Chem. Phys. **206**, 1610-1618 (2005).
[3] S. Ludwigs, G. Krausch, G. Reiter, M. Losik, M. Antonietti, H. Schlaad: Structure formation of polystyrene-block-poly(γ-benzyl L-glutamate) in thin films. Macromolecules **38**, 7532-7535 (2005).

Polymer Synthesis

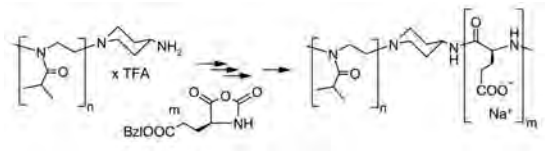
The modification of 1,2-polybutadienes through free-radical addition of mercaptans is a versatile strategy for the generation of a toolbox of functional polymers. However, it was found that the process suffers from a side reaction, namely formation of six-member cyclic units along the backbone. This reaction affects the degree of functionalization but not the molecular-weight distribution of a polymer sample **[4, 10]**.

Functional homopolymers and block copolymers carrying carboxylic acid, amine, ethylene glycol, perfluoroalkyl groups and also biohybrids with pendent amino acid, dipeptide, or glucose units (**Scheme 1**) have so been prepared **[4, 12, 13]**.



Scheme 1: Synthesis of a glucose-grafted block copolymer (glycopolymer) through the radical addition pathway [12].

A combination of cationic and anionic ring-opening polymerization techniques was applied for the synthesis of well-defined double stimuli-responsive biohybrid block copolymers based on poly(2-isopropyl-2-oxazoline) (responding to a change in temerature) and poly(L-glutamate) (responding to a change in pH). Key steps are the preparation of an ω-(ammonium trifluoroacetate)-poly(2-isopropyl-2-oxazoline) and the subsequent ammonium-mediated polymerization of γ-benzyl L-glutamate N-carboxyanhydride (**Scheme 2**) **[8]**.



Scheme 2: Synthesis of poly(2-isopropyl-2-oxazoline)-block-poly(sodium L-glutamate) [8].

Structure Formation

Novel biohybrid amphiphiles prepared through the radical addition pathway could be directly dispersed in organic or in aqueous media, leading to the formation of worms and vesicles **[12, 13]**.

The amphiphilic glycopolymer with the chemical structure shown in Scheme 1 self-assembles into sugar-containing polymer vesicles or "glycosomes" (**Fig. 1a**) being 200-500 nm in diameter **[12]**. Much larger aggregates are formed by peptide-grafted polybutadiene-*block*-poly(ethylene oxide)s in water. Addition of hydrophobic peptides shifts the morphologies towards lower curvature structures, namely from spherical micelles to giant worm micelles and vesicles (**Fig. 1b**). Also helical superstructures arise from the chiral peptide interactions inside the hydrophobic core **[13]**.

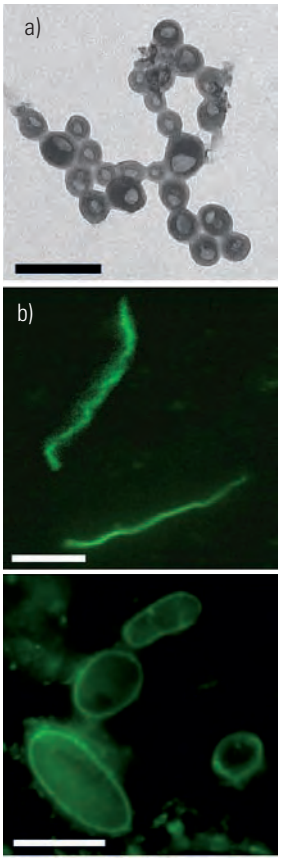


Fig. 1a): Transmission electron micrograph of collapsed glucose-grafted polymer vesicles ("glycosomes") (scale bar = 200 nm) [12], b): confocal fluorescence micrographs of giant peptide-grafted worms and vesicles (scale bar = 5 μm) [13].

Unexpectedly, aqueous solutions of poly(2-isopropyl-2-oxazoline)-*block*-poly(sodium L-glutamate)s produce coagulate when heated above the cloud point of poly(2-isopropyl-2-oxazoline) (~40 °C). Micron-sized coagulate particles are spherical in shape, constructed of long fibrils with a diameter of a few tens of nanometers (**Fig. 2**). Such type of hierarchical structure is also observed for poly(2-isopropyl-2-oxazoline) homopolymers. The mechanism of structure formation is not fully understood yet **[15]**.

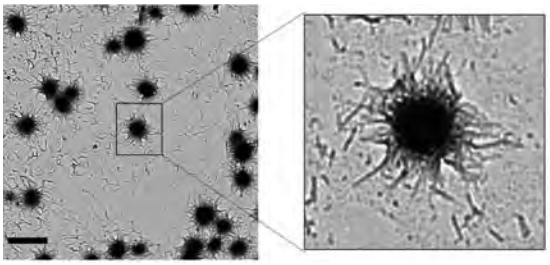


Fig. 2: Transmission electron micrograph of coagulate particles formed by a poly(2-isopropyl-2-oxazoline)-block-poly(sodium L-glutamate) (scale bar = 5 µm) [15].

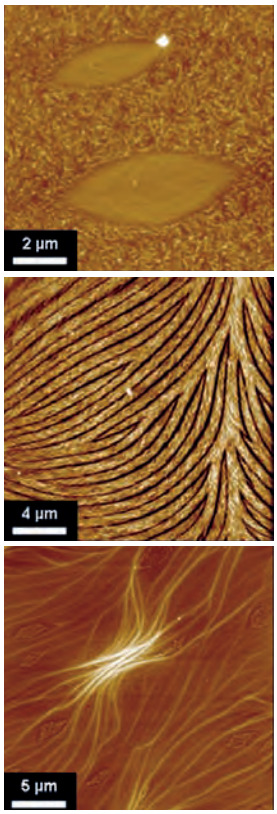


Fig. 3: Scanning force micrographs of a thin film of polystyrene-block-poly(γ-benzyl L-glutamate), solvent-annealed for 3.5, 22.5, and 42 hours (from top to bottom) [3].

Solvent-cast films of polystyrene-*block*-poly(γ-benzyl L-glutamate) usually have a hexagonal-in-lamellar hierarchical superstructure. The preferential formation of lamellae (the intersheet spacing being in the range of a few tens of nanometers) is related to the stiffness of the polypeptide layer. Driven by dipole-dipole interactions, the polypeptide helices are usually arranged in an anti-parallel orientation and densely packed into a two-dimensional hexagonal array. Helices are usually folded but can be fully stretched, depending on the hydrogen-bonding ability of the casting solvent **[9]**.

Structures with a higher level of hierarchical ordering were observed for solvent-annealed thin films of polystyrene-*block*-poly(γ-benzyl L-glutamate) on a silicon substrate. On the smallest length-scale, the structure was found to be built of short ribbons or lamellae of interdigitated polymer chains. Depending on the time of solvent annealing, different ordered structures on the micrometer length-scale could be observed (**see Fig. 3**). So far, a comprehensive picture of the processes involved in the formation of these structures is lacking **[3]**.

H. Schlaad, I. Below, M. Gräwert, A. Greß,
Z. Hordyjewicz, J. Justynska, M. Meyer, L. You
helmut.schlaad@mpikg.mpg.de

[4] J. Justynska, Z. Hordyjewicz, H. Schlaad: Toward a toolbox of functional block copolymers via free-radical addition of mercaptans. Polymer **46**, 12057-12064 (2005).
[5] A. F. Thünemann, D. Schütt, R. Sachse, H. Schlaad, H. Möhwald: Complexes of poly(ethylene oxide)-block-poly(L-glutamic acid) and diminazene. Langmuir **22**, 2323-2328 (2006).
[6] T. Krasia, H. Schlaad: Poly[2-(acetoacetoxy)-ethyl methacrylate]-based hybrid micelles. ACS Symp. Ser. **928**, 157-167 (2006).
[7] H. Schlaad: Solution properties of polypeptide-based copolymers. Adv. Polym. Sci. **202**, 53-73 (2006).
[8] M. Meyer, H. Schlaad: Poly(2-isopropyl-2-oxazoline)-poly(L-glutamate) block copolymers through ammonium-mediated NCA polymerization. Macromolecules **39**, 3967-3970 (2006).
[9] H. Schlaad, B. Smarsly, I. Below: Solid-state structure of polystyrene-block-poly(γ-benzyl L-glutamate): Helix folding versus stretching. Macromolecules **39**, 4631-4632 (2006).
[10] J. Justynska, Z. Hordyjewicz, H. Schlaad: New functional diblock copolymers through radical addition of mercaptans. Macromol. Symp. **240**, 41-46 (2006).
[11] S. Lecommandoux, H.-A. Klok, H. Schlaad: Self-assembly of linear polypeptide-based block copolymers. In M. Lazzari, G. Liu, S. Lecommandoux, Eds.: Block copolymers in nanosciences, Wiley-VCH: Weinheim, 2006, pp. 117-150.
[12] L. You, H. Schlaad: An easy way to sugar-containing polymer vesicles or glycosomes. J. Am. Chem. Soc. **128**, 13336-13337 (2006).
[13] Y. Geng, D. E. Discher, J. Justynska, H. Schlaad: Grafting short peptides onto polybutadiene-block-poly(ethylene oxide): A new platform for self-assembling hybrid amphiphiles. Angew. Chem. Int. Ed. **45**, 7578-7581 (2006).
[14] J. Justynska, PhD thesis, University of Potsdam, 2005.
[15] M. Meyer, PhD thesis, University of Potsdam, 2006.

Polymer-Bioconjugates as Macromolecular LEGO®-Bricks

Hans G. Börner 15.09.1970
1996: Diploma, Chemistry (Philipps-Universität Marburg)
Thesis: Applying the Concept of Large Counter Cations to Metal Free Anionic Polymerization of Acrylates and Meth Acrylates
1997-2000: Ph.D, Macromolecular Chemistry (Philipps-Universität Marburg)
Thesis: Synthesis of Novel Phosphine Substituted Block Copolymers and Application as Building Blocks for Nano Reactors
2000-2002: Postdoctoral Fellow (Carnegie Mellon University, Pittsburgh, USA)
Since 2002: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
2002: Visiting Researcher (Department of Biochemistry, Stellenbosch University, South Africa)

Controlling interactions in synthetic polymers as precisely as in proteins would have a strong impact on polymer science. Advanced structural and functional control can lead to rationally designable, integrated nano- and microstructures. To achieve this we exploit properties of sequence-defined oligopeptides. By incorporating these as monodisperse segments into synthetic polymers, we learn how to program structure formation **[1]**, interactions with biosystems **[2]** and manipulation of crystal surfaces **[3, 4]**.

Methodologies to Synthesize Bioconjugates

In order to selectively introduce peptides into synthetic polymers, new routes had to be developed, applying two main strategies:

i. Polymerization strategies, in which the polymer segment is synthesized in the presence of the peptide **[5]**. This approach includes the sequence specific introduction of an initiator or chain transfer functionality to a peptide. The resulting macroinitiator or macrotransfer agent was applied in controlled radical polymerization (CRP) processes, such as atom transfer radical polymerization (ATRP) **[6]** and reversible addition-fragmentation chain transfer polymerization (RAFT) **[7]**. This allows the synthesis of well-defined conjugates with controllable molecular weight and polydispersties as low as 1.1.

ii. Coupling approaches including the regio-selective ligation of a polymer that has a defined chain-end functionality with a complementary functionality of a peptide. To diversify this route, different strategies, allowing the introduction of chain-end functionalities into synthetic polymers were investigated. CRP was combined with either protected functional initiators **[8]** or specific chain-end-group transformations **[9]**. In addition, different ligation techniques, e.g. the highly specific click-reaction, were applied **[10]**.

Bioinspired Formation of Structure and Function

The resulting bioconjugates allow for the rather direct realization of bio-inspired polymer science. Peptides combine self-assembly properties with the potential to actively interact with biological systems. Hence, peptide-polymer conjugates can be used to program structure formation in polymeric materials.

We exploited the biological concept of peptide-guided structure formation for the organization of synthetic polymers, using different peptide-based organizer units (**Fig. 1**) **[1]**. Particularly, the peptide organization in form of the β-sheet secondary structure motif was investigated. Thus, highly attractive, anisometric tape, fibrillar or fiber-like nanostructures can be accessed. These are important structural and functional elements in both native and synthetic materials that provide anisotropic strength and elasticity or directed transport.

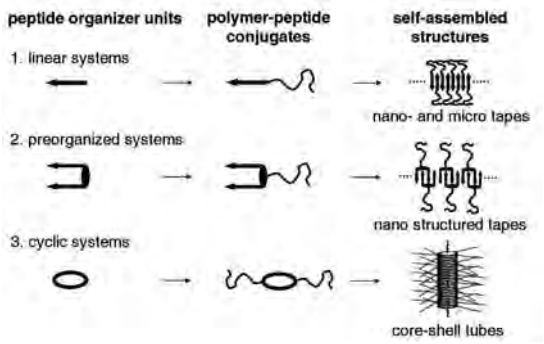


Fig. 1: Illustration of the concept of peptide-guided organization of synthetic polymers.

As outlined in **Fig. 1** the peptide organizer segment in a peptide-polymer conjugate induces and controls the microstructure formation. Thus, different peptide organizers result in different structures, ranging from macro- to nanotapes and nanotubes (**Fig. 2**) **[8, 11-14]**.

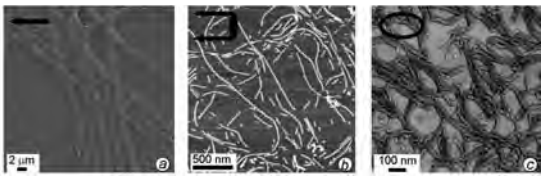


Fig. 2: Peptide-guided self assembly of synthetic polymers: a) PEO-tapes (SEM), b) PEO nanotapes (AFM, height) and c) pBA hollow fibers (AFM, phase).

Representative of the other projects, two examples will be discussed in detail, illustrating the potentials of the peptide-guided organization for materials science:

Linear peptide organizers: The synthesis of extended and robust nanofibres, interesting for material science, requires peptides with strong tendencies to form stable aggregates. These, however, are usually difficult to access. Recently, the SWITCH-strategy of integrating defined defects into the peptide backbone was developed to overcome these obstacles. The defects, referred to as "switch"-segments, temporarily suppress the aggregation tendency of a peptide. The native peptide can be reestablished via a selective rearrangement in the switch segments, restoring the aggregation tendency.

Such switch segments have been shown to be highly useful for the peptide-guided organization of synthetic polymers (**Fig. 3a**), as the rate of switching can be adjusted to control the aggregation kinetics **[11,13]**. Using the switch-strategy, PEO-peptide conjugates in water organized into macrotapes with up to several millimeters in length (**Fig. 2a, 3b**) **[11]**.

References:
[1] Börner, H. G.: Functional Polymer-Bioconjugates as Molecular LEGO®-Bricks. Macromol. Chem. Phys. **208**, 124-130, (2007).
[2] Hartmann, L., Krause, E., Antonietti, M., Börner, H. G.: Solid-Phase Supported Polymer Synthesis of Sequence Defined, Multifunctional Poly(amidoamines). Biomacromolecules **7**, 1239-1244, (2006).
[3] Page, M. G., Nassif, N., Börner, H. G., Antonietti, M., Cölfen, H.: Mesoporous calcite by polymer templating. (2006) submitted.
[4] Ma, Y., Börner, H. G., Hartmann, J., Cölfen, H.: Synthesis of DL-alanine hollow tubes and core-shell mesostructures. Chem. Eur. J. **12**, 7682-7688, (2006).
[5] ten Cate, M. G. J., Börner, H. G.: Conjugates of polymers and sequence-defined polypeptides via controlled radical polymerization. ACS Symp. Ser. "Controlled/Living Radical Polymerization: From Synthesis to Materials" **944**, 198-214, (2006).

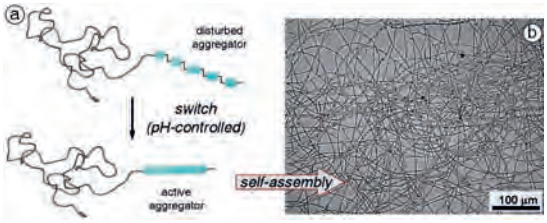


Fig. 3: Schematic presentation of the pH-triggered organization of synthetic polymers (a) and light microscopy of the self-assembled PEO-macro tapes (b).

Moreover, the switch proceeds also in organic solvents, allowing the assembly of poly(butyl acrylate) into helical-tapes with a left-handed twist **[13]**. These protostructures exhibit distinct entanglement into soft organo-gels (**Fig. 4**). This example shows that structural control provides control over functions, similarly to the constitution of functions in proteins. The helical tapes can be seen as nano-springs and exciting micromechanic properties are expected.

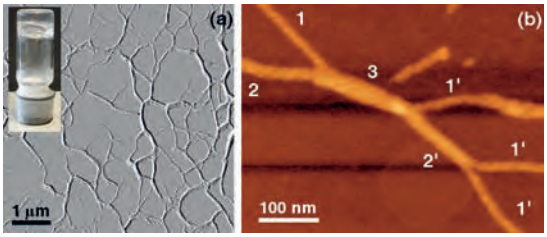


Fig. 4: AFM of the organo-gel, formed by assembly of a poly(butyl acrylate)-peptide conjugate (a); macroscopic gel (a, inset); cross-links in the gel showing single tapes with helical twist (1,1'), dual tapes (2, 2') and tipple tapes (3) (b).

Mimicking Biomaterials

Biological inorganic-organic materials from bones to glass sponges are high performance, fiber reinforced composites, with purpose-adapted properties. For instance, the glass sponge *Euplectella sp.*, one of the most primitive animals in existence, realizes integrated composite materials based on glass with outstanding mechanical properties.

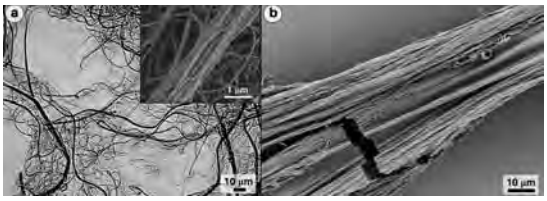


Fig. 5: Self-assembled nanofiber-reinforced silica fibers (light microscopy (a), SEM (a,inset) and continuously produced biomimetic silica fibers exhibiting fracture (b)).

To mimic the biosilification process, peptide-PEO nanotapes (**Fig. 2b**) **[12]** were applied in a sol-gel silica synthesis. During a self-assembly-silification process, nanofiber-reinforced silica fibers spontaneously formed (**Fig. 5a**). Detailed analysis of the material reveals a hierarchical order. The process is still not fully understood. However, apparently, the functionalities of the PEO-peptide-tapes guide the silification process towards the formation of rather uniform proto-composite fibers that further tend to form bundles (**Fig. 5a, inset**).

Preliminary experiments show that a continuous spin process can be performed, which results in fiber-bundles whose fracture behavior indicates interesting mechanical properties (**Fig. 5b**).

Biomedical Applications

The development of defined peptide-polymer conjugates allows addressing pharmacological and biomedical issues **[15]**. However, to avoid the inherent immunogenicity of peptides, a novel synthesis route to linear poly(amido amines) (PAAs) was developed **[2]**. This enables one to synthesize monodisperse PAAs with a defined monomer sequence. The cationic character (balance of *tert., sec.,* and *prim.* amine groups) of the PAA segment can be fine-tuned with monomer resolution, making the PAAs – if conjugated to PEO – highly interesting for gene delivery. PEO-PAAs are well-defined model compounds with sharp property profiles allowing for the correlation of e. g. the cationic balance with DNA complexation and compression properties (**Fig. 6**) as well as membrane translocation and transfection activities.

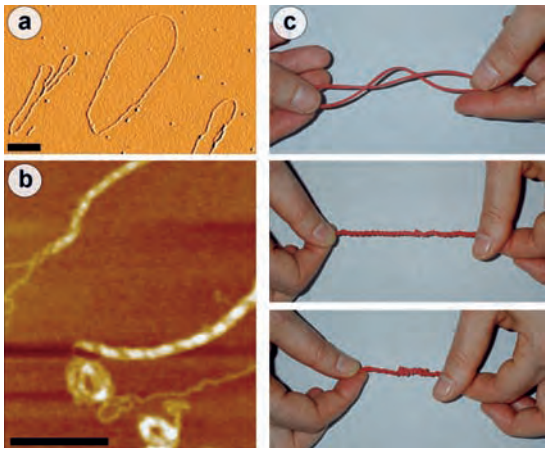


Fig. 6: Induction of super-coiling in plasmid dsDNA (a,b) and illustration of the process by a rubber band (c); (Expanded DNA using PEO-PAAs with tertiary amines (a) and super-coilded DNA using PEO-PAAs with a mixture of sec. and prim. amines (b)(AFM, scale bar = 200 nm)).

Outlook

It is predictable that polymer chemistry with its inherent molecular weight distributions will evolve to macromolecular chemistry with precisely defined molecules. Hence, the synthesis of fully synthetic, monodisperse polymers with defined monomer sequences will be the upcoming challenge in polymer science. Completely unnatural polymer classes might be developed, which combine novel units capable of specific molecular recognition with new monomer alphabets to fine-tune secondary interactions along linear polymer chains.

H. G. Börner, M. ten Cate, L. Hartmann, Y. Yagci,
J. Hentschel, S. Kessel, H. Hahn; J. Brandt, K. Ostwald.
hans.boerner@mpikg.mpg.de

[6] Rettig, H., Krause, E., Börner, H. G.: Atom transfer radical polymerization with polypeptide initiators: A general approach to block copolymers of sequence-defined polypeptides and synthetic polymers. Macromol. Rapid Commun. **25**, 1251-1256, (2004).
[7] ten Cate, M. G. J., Rettig, H., Bernhardt, K., Börner, H. G.: Sequence-Defined Polypeptide-Polymer Conjugates Utilizing Reversible Addition Fragmentation Transfer Radical Polymerization. Macromolecules **38**, 10643-10649, (2005).
[8] ten Cate, M. G. J., Severin, N., Börner, H. G.: Self-Assembling of Peptide-Polymer Conjugates Comprising (D-alt-L)-Cyclopeptides as Aggregator Domains. Macromolecules **39**, 7831-7838, (2006).
[9] Lutz, J.-F., Börner, H. G., Weichenhan, K.: Combining ATRP and Click Chemistry: an "Universal" Method for Preparing End-Functional Polymers. Macromol. Rapid Commun. **26**, 514-518, (2005).
[10] Lutz, J.-F., Börner, H. G., Weichenhan, K.: Combining ATRP and "click" chemistry: a Promising Platform Towards Functional Biocompatible Polymers and Polymer Bioconjugates. Macromolecules **39**, 6376-6383, (2006).
[11] Hentschel, J., Krause, E., Börner, H. G.: Switch-peptides to Trigger the Peptide Guided Assembly of Poly(ethylene oxide)-Peptide Conjugates into Tape Structures. J. Am. Chem. Soc. **128**, 7722 - 7723, (2006).
[12] Eckhardt, D., Groenewolt, M., Krause, E., Börner, H. G.: Rational design of oligopeptide organizers for the formation of poly(ethylene oxide) nanofibers. Chem. Commun. 2814-2816, (2005).
[13] Hentschel, J., Börner, H. G.: Peptide-Directed Microstructure Formation of Polymers in Organic Media. J. Am. Chem. Soc. **128**, 14142-14149, (2006).
[14] Börner, H. G., Schlaad, H.: Bioinspired functional block copolymers. Soft Matter **3**, 394-408, (2007).
[15] Dünne, A. A., Börner, H. G., Kukula, H., Schlaad, H., Werner, J. A., Antonietti, M.: Block copolymer carrier systems for translymphatic chemotherapy of lymph node metastases. submitted, (2006).

Biomimetic Mineralization

Helmut Cölfen 24.07.1965
1991: Diploma, Physical Chemistry (University of Duisburg)
Thesis: Analytical Ultracentrifugation of Gels
1993: PhD, Physical Chemistry (University of Duisburg)
Thesis: Analytical Ultracentrifugation of Gels
1993-1995: Postdoc (National Center 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
Since 2004: Private Docent; University of Potsdam

This project investigates polymer additive controlled mineralization in an attempt to apply principles from biomineralization processes. This includes the understanding of crystallization and biomineralization principles as well as their adaptation to synthetic materials. In recent years, it became evident that many crystallization processes do not follow the classical path of atom/ion/molecule assembly to a single crystal but instead proceed via the self organization of nanoparticles **[1-4]**. Such self organization processes can be directed in a versatile way by the application of polymer additives. If block copolymers are used, the individual polymer blocks can even be "programmed" to optimally realize a desired function like adsorption on a specific crystal face, temporary stabilization in the solvent etc. It is desirable to work in water as solvent and thus, a useful block copolymer design is to use one water soluble block not interacting with crystal surfaces like poly(ethylene oxide) and another block, which selectively interacts with crystal faces. Especially active for adsorption onto minerals like $CaCO_3$ or $BaCO_3$ are acidic polyelectrolyte blocks like polyphosphonates. We have synthesized a variety of such block copolymers using various radical polymerization strategies and successfully applied these molecules as crystallization additive **[5]**.

Especially intriguing structures were obtained when a stiff phosphonated block was applied, which selectively attached to (110) faces of $BaCO_3$. In this case, tectonic arrangement of elongated nanoparticles to helical superstructures was achieved, although the polymer was racemic and $BaCO_3$ not chiral, and the formation mechanism could be revealed **[6]**. Similar addressing of selected $CaCO_3$ calcite faces by block copolymers leads to the formation of thin $CaCO_3$ sheets, which form pancake-like structures **[7]**.

This investigation showed that the epitaxial view of polymer adsorption onto a crystal face is too simplified and that factors like charge density, polymer flexibility etc. also play a role onto which crystal surface the polymer will adsorb. These investigations were extended to the formation of $CaCO_3$ microrings **[8]** or ZnO nanorings and disks **[9]**. If a sophisticated multi-shell polymer particle architechture is used as a template, a single polymer microgel particle could be used to template an entire aragonite nanoparticle super-structure. Not only the synthesis of the aragonite $CaCO_3$ polymorph is unusual, it is further remarkable that all nanoparticles in the superstructure are crystallographically connected **[10]**.

The self organization of nanoparticles in crystallographic register was of especial interest in this project as it is a non-classical crystallization pathway, by which single crystals can be formed by nanoparticle superstructure intermediates. The underlying mechanism is the so called "Oriented Attachment" in which nanoparticles self organize within crystallographic register. Subsequently, they may fuse at high energy crystal surfaces and a single crystal can be formed gaining energy by elimination of two high energy surfaces. Such mechanism could be identified for $CaCO_3$ in presence of polymers **[11]** or even without polymer additives by the adsorption of ammonia ions **[12]** as well as for $BaSO_4$ in presence of poly(acrylate) polymer additives **[13, 14]**. For the $BaSO_4$ fibers, the formation mechanism was investigated in detail revealing polymer interaction already with the Ca^{2+} ions, formation of amorphous precursor particle aggregates, nanoparticle crystallization and oriented attachment with subsequent nanoparticle fusion to single crystalline defect free nanofibers **[13, 14]**.

The oriented attachment of nanoparticles can not only occur in one **[13, 14]** or two **[11, 12]** but also in three dimensions forming so-called mesocrystals, which are nanoparticle superstructures in crystallographic register, single crystalline scattering behaviour and often a facetted morphology **[15-18]**. DL-alanine proved to be a good model system for mesocrystal formation as the molecule already has a dipole moment and dipole-dipole interactions can be used to structure DL-alanine nanocrystals in crystallographic register to a mesocrystal **[16, 17]**. In addition, the solubility of an amino acid can be controlled in an easy way by pH variations and the conditions for mesocrystal formation could be identified as those with high supersaturation and thus nucleation burst of a large number of nanoparticle building units, whereas low supersaturation led to molecule mediated crystallization along the classical crystallization pathway **[17]**.

Mesocrystals can also be formed for classical mineral systems like $CaCO_3$, however, only in presence of a polymer additive **[15, 18 & Figure 1]**. Selective adsorption of the polyacid polymer additive poly(styrene sulfonate) to the charged (001) faces of calcite leads to nanoparticles with positive and negative charges on the opposite faces **[18]** followed by a self organization of the calcite nanoplatelets in crystallographic register to form the mesocrystal. The transition from single crystal to mesocrystal to polycrystal seems to be continuous and can be adjusted in a simple way via the polymer/$CaCO_3$ ratio as shown in Figure 1 with the typical calcite rhomboeder formed at the lowest polymer and $CaCO_3$ concentration, which are closest to the classical crystallization conditions for $CaCO_3$ (**Fig. 1a, 18**)

References:
[1] Cölfen, H. and Yu, S.H. MRS Bulletin 30, 727-735 (2005).
[2] Cölfen, H. and Antonietti, M. Angew. Chem. Int. Ed. **44**, 5576-5591 (2005).
[3] Niederberger, M. and Cölfen, H. Phys. Chem. Chem. Phys. **8**, 3271-3287 (2006).
[4] Yu, S.H. and Cölfen, H. In N.A. Kotov (Ed.) Nanoparticle Assemblies and Superstructures, 269-338 (2006), Taylor & Francis.
[5] Wang, T., Rother, G. & Cölfen, H. Macromol. Chem. Phys. **206**, 1619-1629 (2005).
[6] Yu, S.H., Cölfen, H., Tauer, K. and Antonietti, M. Nature Mater. **4**, 51-55 (2005).
[7] Chen, S.F., Yu, S.H., Wang, T.X., Jiang, J., Cölfen, H., Hu, B. and Yu, B. Adv. Mater. **17**, 1461-1465 (2005).

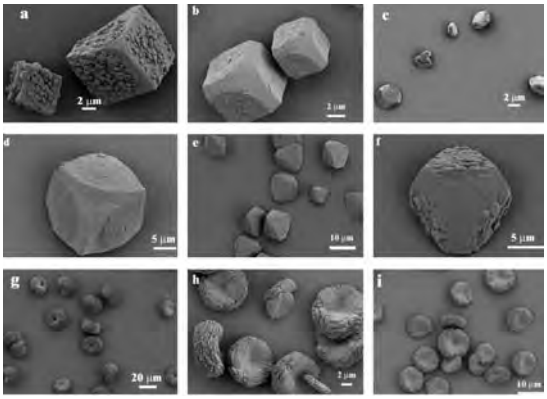


Fig. 1: Typical SEM images of calcite mesocrystals obtained on a glass slip by the gas diffusion reaction after 1 day in 1 mL of solution with different concentrations of Ca^{2+}] and polystyrene-sulfonate: a) [Ca^{2+}] = 1.25 mmol/L, [PSS] = 0.1 g/L; b) [Ca^{2+}] = 1.25 mmol/L, [PSS] = 0.5 g/L; c) [Ca^{2+}] = 1.25 mmol/L, [PSS] = 1.0 g/L; d) [Ca^{2+}] = 2.5 mmol/L, [PSS] = 0.1 g/L; e) [Ca^{2+}] = 2.5 mmol/L, [PSS] = 0.5 g/L; f) [Ca^{2+}] = 2.5 mmol/L, [PSS] = 1.0 g/L; g) [Ca^{2+}] = 5 mmol/L, [PSS] = 0.1 g/L; h) [Ca^{2+}] = 5 mmol/L, [PSS] = 0.5 g/L; i) [Ca^{2+}] = 5 mmol/L, [PSS] = 1.0 g/L. (From Ref. 18)

Another target of our research is the investigation of biomineralization principles. In the field, amorphous precursor phases are recently reported for an increasing number of biominerals. Even liquid precursors are discussed and we investigated for amino acid model systems, under which conditions, liquid precursors can be formed and how they can be applied to generate crystals with complex shape in a very easy way **[19]**. In addition, unstable amorphous $CaCO_3$ could be synthesized with a simple phosphorylated sugar molecule (phytic acid) and kept stable in aqueous environment for weeks demonstrating the use of amorphous precursor phases as material reservoir **[20]**.

Applying amorphous precursor particles as precursors in a biomimetic mineralization reaction inside the organic demineralised matrix of nacre as a scaffold, the platelet-like mineral structure of the original nacre was obtained (**Fig. 2, 21**). This suggests this system as suitable model system to study the details of the mineralization process and to learn about the natural nacre archetype **[21]**.

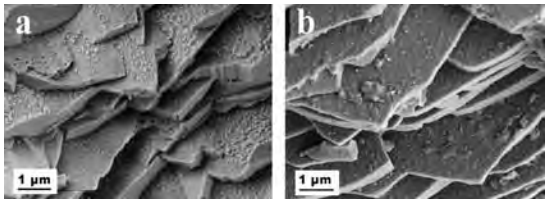


Fig. 2: SEM micrographs of fracture surfaces of (a) synthetic nacre; (b) original nacre from Haliotis laevigata.(From Ref. 20)

Indeed, a high resolution TEM investigation of natural nacre revealed an amorphous layer on top of the aragonite platelets **[22]** similar to synthetic aragonite **[10]** supporting amorphous precursor phases in the synthesis of nacre.

The role of amorphous precursor phases in the morphosynthesis of crystals was also investigated for the DL-alanine model system. Here, hollow alanine needles could be obtained by a dissolution-recrystallization process of amorphous precursor nanoparticle aggregates **[23]**. In addition, we introduced an improved method for slow $CaCO_3$ crystallization without ion contamination **[24]** as it turned out that ammonia ions can act as active additive in $CaCO_3$ crystallization **[12]**.

Also, dynamic pattern formation in crystallization was investigated. When phosphonated block copolymers **[5]** were used as additives for the crystallization of $BaCO_3$, a reaction-diffusion system could be established under certain experimental conditions leading to a concentric ring pattern typical of a Belousov-Zhabotinsky reaction. This reaction was described here first, for a two phase system implementing self organizing nanocrystal structures. The key step was the autocatalytic formation of a Ba-polymer complex as a precursor to amorphous nanoparticle formation, which was followed by particle crystallization and self organization **[25]**.

Overall, our research has revealed that polymer controlled crystallization is useful to study basic crystallization mechanisms, generate crystals with complex structure and form or mimic and understand biomineralization principles. Especially the non-classical particle mediated crystallization paths are highly interesting for future studies, as so far, only little is known about these self organization mechanisms.

H. Cölfen, M. Barth, N. Nassif, T. Wang, A.W. Xu, Y. Ma, M. Page, N. Gehrke, D. Gebauer
Coelfen@mpikg.mpg.de

[8] Gao, Y.X.; Yu, S.H.; Cong, H.; Jiang, J.; Xu, A.W.; Dong, W. F. and Cölfen, H. J. Phys. Chem. B **110**, 6432-6436 (2006).
[9] Peng, Y., Xu, A.W., Deng, B., Antonietti, M. and Cölfen, H. J. Phys. Chem. B **110**, 2988-2993 (2006).
[10] Nassif, N., Gehrke, N., Pinna, N., Shirshova, N., Tauer, K., Antonietti, M. and Cölfen, H. Angew. Chem. Int. Ed. **44**, 6004-6009 (2005).
[11] Xu, A.W., Antonietti, M., Cölfen, H. and Fang, Y.P. Adv. Funct. Mater. **16**, 903-908 (2006).
[12] Gehrke, N., Cölfen, H., Pinna, N., Antonietti, M. & Nassif, N. Cryst. Growth Design **5**, 1317-1319 (2005).
[13] Wang, T. and Cölfen, H. 1. Kinetics and Solution Analysis. Langmuir **22**, 8975-8985 (2006).
[14] Wang, T., Reinecke, A. and Cölfen, H. 2. Crystallization Mechanisms. Langmuir **22**, 8986-8994 (2006).
[15] Wang, T., Cölfen, H. and Antonietti, M. J. Amer. Chem. Soc. **127**, 3246-3247 (2005).
[16] Wohlrab, S., Pinna, N., Antonietti, M. and Cölfen, H. Chem. Eur. J. **11**, 2903-2913 (2005).
[17] Ma, Y., Cölfen, H. and Antonietti, M. J. Phys. Chem. B **110**, 10822-10828 (2006).
[18] Wang, T., Antonietti, M. and Cölfen, H. Chem. Eur. J. 12, 5722-30 (2006).
[19] Wohlrab, S., Cölfen, H. and Antonietti, M. Angew. Chem. Int. Ed. **44**, 4087-4092 (2005).
[20] Xu, A.W., Yu, Q., Dong, W.F., Antonietti, M. and Cölfen, H. Adv. Mater. **17**, 2217-2221 (2005).
[21] Gehrke, N., Nassif, N., Pinna, N., Antonietti, M., Gupta, H. S. and Cölfen, H., Chem. Mater. **17**, 6514-6516 (2005).
[22] Nassif, N., Pinna, N., Gehrke, N., Antonietti, M., Jäger, C. and Cölfen, H. Proc. Nat. Acad. Sci. USA **102**, 12653-5 (2005).
[23] Ma, Y., Börner H.G., Hartmann, J. and Cölfen, H. Chem. Eur. J. **12**, 7882-8 (2006).
[24] Page, M. G. and Cölfen, H. Cryst. Growth Design 6, 1915-1920 (2006).
[25] Wang, T., Xu, A.-W. & Cölfen, H. Angew. Chem. Int. Ed. **45**, 4451-4455 (2006).

Organic Chemistry Meets Inorganic Materials Synthesis

Markus Niederberger 10.06.1970
1996: Diploma, Chemistry [Swiss Federal Institute of Technology (ETH) Zürich, Switzerland]
2000: PhD in Chemistry (ETH Zürich)
Thesis: Synthesis and Characterization of Novel Micro- and Nanostructured Vanadium, Molybdenum, and Iron Oxides
2001-2002: Postdoc (University of California at Santa Barbara)
2002-2006: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
2007: Assistant Professor (ETH Zürich, Department of Materials)

1. Introduction

Sol-gel routes to metal oxide nanoparticles in organic solvents under exclusion of water represent a versatile alternative to aqueous methods. In comparison to the complex aqueous chemistry, nonaqueous processes offer the possibility to better understand and to control the reaction pathways on a molecular level, enabling the synthesis of nanomaterials with high crystallinity and well-defined and uniform particle morphologies **[1]**.

2. Synthesis

The most popular metal oxide precursors are metal halides, metal acetylacetonates, and metal alkoxides, and mixtures thereof for multi-metal oxides. The solvents vary from alcohols to amines, nitriles, ketones and aldehydes, and also include mixtures of these solvents **[1]**. Depending on the reactivity of the metal oxide precursor with the respective solvent, the synthesis temperature typically ranges from about 50 °C to 250 °C. Procedures at temperatures higher than or close to the boiling point of the organic solvent are performed in steel autoclaves with Teflon liners.

These nonaqueous and surfactant-free sol-gel procedures gave access to a wide variety of metal oxide nanoparticles including TiO_2, CeO_2, ZrO_2, HfO_2, In_2O_3, Ga_2O_3, Nb_2O_5, Ta_2O_5, SnO_2, ZnO, WO_x, FeO_x, $BaTiO_3$, $SrTiO_3$, $(Ba,Sr)TiO_3$, $BaZrO_3$, $Pb(Zr,Ti)O_3$, $LiNbO_3$, $NaNbO_3$, $NaTaO_3$, or $BaSnO_3$ **[1]**.

As selected examples **Fig. 1** displays TEM overview images of indium oxide, tin oxide, indium tin oxide and zinc oxide nanoparticles. The indium oxide nanoparticles in **Fig. 1a** were obtained from indium acetylacetonate in benzylamine at 200 °C. The same process can also be used for iron, gallium and zinc oxide nanoparticles **[2]**. Fairly monodisperse tin oxide nanocrystals in the size range of 3-6 nm were prepared from tin tetrachloride and benzyl alcohol at 100-110 °C (**Fig. 1b**) **[3]**. The high dispersibility of these nanoparticles made it possible to assemble them into mesoporous materials (**Fig. 1b**, inset) by applying block copolymers as templates and the evaporation-induced self-assembly process **[3]**. Indium tin oxide was obtained from indium acetylacetonate and tin *tert*-butoxide in benzyl alcohol at 200 °C **[4]**. Obviously the reactivity of these two precursors in benzyl alcohol matched each other in a way that formation of solid solution takes place. The nanoparticles are crystalline with diameters of 5-10 nm (**Fig. 1c**). Without further annealing they show good electrical conductivity **[4]**. Another low-temperature route to metal oxides involves the solvothermal reaction of metal acetylacetonates with acetonitrile at 100 °C. Using this approach, indium and zinc oxide nanoparticles were synthesized **[5]**. Whereas In_2O_3 consisted of individual nanoparticles with a spherical morphology and a small size distribution of 3-6 nm, the ZnO nanoparticles had sizes of 15-85 nm (**Fig. 1d**) and were sometimes composed of a highly oriented arrangement of smaller nanocrystallites forming hexagonal, well-faceted mesocrystals (**Fig. 1d**, inset).

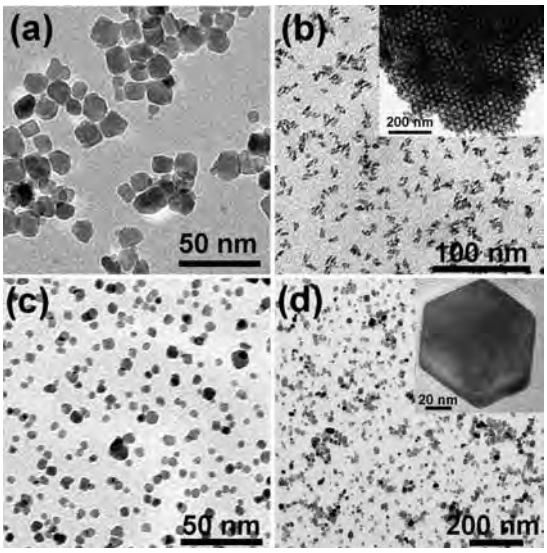
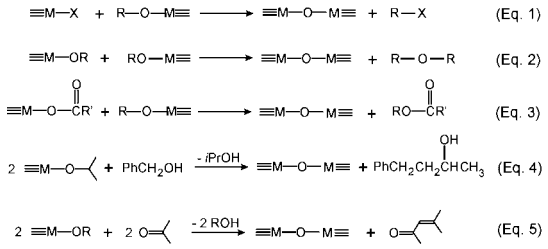


Fig. 1: TEM overview images of selected metal oxide nanoparticles. a) Indium oxide, b) tin oxide (inset: mesoporous SnO_2), c) indium tin oxide, d) zinc oxide (inset: ZnO mesocrystal).

3. Formation and Crystallization Mechanisms

In aqueous sol-gel processes, the oxygen for the oxide formation is provided by the water molecules. In nonaqueous systems, where intrinsically no water is present, the oxygen comes either from the organic solvent or from the organic constituent of the metal oxide precursor **[1]**. The most common condensation steps leading to a metal-oxygen-metal bond, the basic "molecular" unit of metal oxides, are summarized in **Scheme 1**. Eq. 1 displays the condensation between metal halides and metal alkoxides (formed *in situ* upon the reaction of metal halides with alcohols) under release of an alkyl halide. Ether elimination (Eq. 2) is the result of the reaction between two metal alkoxides, ester elimination between metal carboxylates and metal alkoxides (Eq. 3). In selected cases a more sophisticated pathway was found, where the M-O-M bond formed upon reaction of benzyl alcohol with the isopropoxy ligand of the metal isopropoxide (Eq. 4) **[1]**. Ketones as solvent release their oxygen typically by aldol condensation reactions (Eq. 5).

References:
[1] Niederberger, M., Garnweitner, G.: Organic reaction pathways in the nonaqueous synthesis of metal oxide nanoparticles. Chem. Eur. J. **12**, 7282 (2006).
[2] Pinna, N., Garnweitner, G., Antonietti, M., Niederberger, M.: A general nonaqueous route to binary metal oxide nanocrystals involving a C-C bond cleavage. J. Am. Chem. Soc. **127**, 5608 (2005).
[3] Ba, J., Polleux, J., Antonietti, M., Niederberger, M.: Nonaqueous synthesis of tin oxide nanocrystals and their assembly into ordered porous mesostructures. Adv. Mater. **17**, 2509 (2005).
[4] Ba, J., Fattakhova Rohlfing, D., Feldhoff, A., Brezesinski, T., Djerdj, I., Wark, M., Niederberger, M.: Nonaqueous synthesis of uniform indium tin oxide nanocrystals and their electrical conductivity in dependence of the tin oxide concentration. Chem. Mater. **18**, 2848 (2006).
[5] Buha, J., Djerdj, I., Niederberger, M.: Nonaqueous synthesis of nanocrystalline indium oxide and zinc oxide in the oxygen-free solvent acetonitrile. Cryst. Growth Des. **7**, 113 (2007).



Scheme 1: Selected condensation steps in nonaqueous sol-gel processes resulting in the formation of a metal-oxygen-metal bond. Alkyl halide elimination (Eq. 1), ether elimination (Eq. 2), ester elimination (Eq. 3), C-C bond formation between benzylic alcohols and alkoxides (Eq. 4), aldol condensation reactions (Eq. 5).

Although the investigation and classification of these organic reaction mechanisms represent an important progress in nanoparticle synthesis, the ultimate goal of a rational synthesis strategy for inorganic nanomaterials is still far away. The big question of finding a relationship between a particular synthesis system and the final particle morphology remains unanswered. One of the reasons is the poorly understood crystallization process of nanoscale materials. In addition to the classical crystallization mechanism based on the attachment of ions, atoms or molecules to a growing nucleus, particle mediated growth and assembly mechanisms seem to be important, too. These non-classical crystallization pathways involve processes like oriented attachment and mesocrystal formation **[6]**. The complexity of crystallization is nicely represented in the case of indium tin oxide nanoparticles. They do not crystallize in a simple nucleation and growth process during solvothermal treatment, but first form an intermediary phase consisting of aligned nanocrystallites embedded in an organic matrix (**Fig. 2a and b**), followed by the transformation into the bixbyite structure with larger crystallites (**Fig. 2c**) and accompanied by the disappearance of both the organic phase and the superstructure **[7]**.

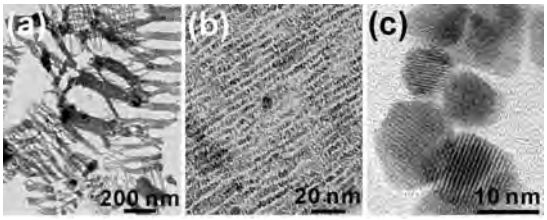


Fig. 2: TEM images of indium tin oxide nanoparticles after different reaction times. a) After 3h, b) after 6h and c) after 24h.

4. Role of the Organic Species: Tungsten Oxide as Case Study

The organic species in the reaction system strongly influence the composition, size, shape, surface properties and even the crystal structure of the inorganic products. Consequently, the organic side bears the potential to control the structural and morphological characteristics. However, this goal can only be achieved, if the role of the organic species is understood on a molecular level and at all stages of the synthesis process. To make first steps in this direction, the influence of different organic solvents and ligands on the particle morphology and assembly behavior of tungsten oxide was investigated. The reaction of tungsten chloride with benzyl alcohol leads to the formation of tungstite nanoplatelets (**Fig. 3a**). If the same process is carried out in the presence of the bioligand deferoxamine, the particle morphology drastically changes, leading to bundles of assembled nanowires (**Fig. 3b**) **[8]**. The nanowires are highly crystalline and exhibit a uniform diameter of about 1.3 nm (**Fig. 3c**). Similar nanowires can be prepared without any additional organic templates by reacting tungsten isopropoxide with benzyl alcohol (**Fig. 3d**) **[9]**. Tungsten chloride and 4-*tert*-butylbenzyl alcohol result in highly ordered ribbon-like structures, composed of parallel columns of stacked nanoplatelets (**Fig. 3e**) **[10]**. It is also possible to get stacks of nanoplatelets in the tungsten chloride-benzyl alcohol system. But in this case, 4-*tert*-butylcatechol has to be added to induce the assembly process (**Fig. 3f**) **[10]**.

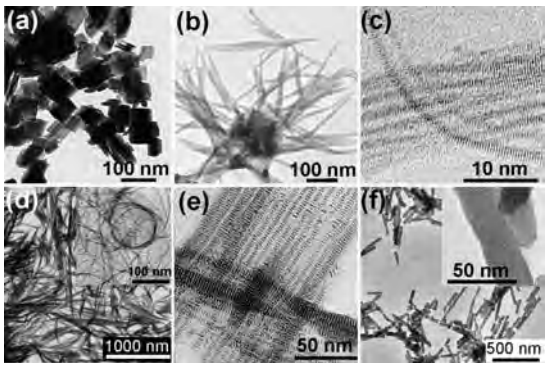


Fig. 3: TEM images of a) tungsten oxide nanoplatelets, b) tungsten oxide nanowire bundles, c) tungsten oxide nanowires, d) tungsten oxide nanowire bundles (inset: individual tungsten oxide nanowires), e) and f) stacks of tungsten oxide nanoplatelets. Details see text.

M. Niederberger, J. Ba, J. Buha, M. Cao, I. Djerdj, G. Garnweitner, R. Rothe, L. Zhang, S. Zhou
markus.niederberger@mpikg.mpg.de

[6] Niederberger, M., Cölfen, H.: Oriented attachment and mesocrystals: non-classical crystallization mechanisms based on nanoparticle assembly. Phys. Chem. Chem. Phys. **8**, 3271 (2006).
[7] Ba, J., Feldhoff, A., Fattakhova Rohlfing, Wark, M., Antonietti, M., Niederberger, M.: Crystallization of indium tin oxide nanoparticles: from cooperative behavior to individuality. Small **3**, 310 (2007).
[8] Polleux, J., Pinna, N., Antonietti, M., Niederberger, M.: Growth and assembly of crystalline tungsten oxide nanostructures assisted by bioligation. J. Am. Chem. Soc. **127**, 15595 (2005).
[9] Polleux, J., Gurlo, A., Barsan, N., Weimar, U., Antonietti, M., Niederberger, M.: Template-free synthesis and assembly of single-crystalline tungsten oxide nanowires and their gas-sensing properties. Angew. Chem. Int. Ed. **45**, 261 (2006).
[10] Polleux, J., Antonietti, M., Niederberger, M.: Ligand and solvent effects in the nonaqueous synthesis of highly ordered anisotropic tungsten oxide nanostructures. J. Mater. Chem. **16**, 3969 (2006).

Mesoporous "Non-Oxidic" Materials

Arne Christian Thomas 07.04.1975
2001: Diploma, Chemistry (Philipps-Universität Marburg)
Thesis: Synthesis of cholestric cellulose derivatives with covalently bonded chromophores and investigation of their optical properties
2003: PhD, Chemistry (Universität Potsdam)
Thesis: Mesoporous silicas by nanocasting – from chiral templates to a new chemistry in pores
2004-2005: Postdoc (University of California, Santa Barbara, USA)
Since 2005: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Nanostructured mesoporous materials have a broad scope of prospects and applications and were extensively studied in recent years. Our research is focused on the development of new or improved "soft" mesoporous materials composed of carbon, carbon nitrides, polymers or organosilicas, in contrast to the recently more often described "hard" mesoporous inorganic metal oxides.

The sustainability of a technical innovation is always accompanied by the question of costs, environmental constraints and accessibility of the required scaffold. Therefore new materials are not only required to have an exceptional performance for the desired application, but also a low cost, non-toxicity and overall environmental compatibility of the respected materials. For many applications, such as catalysis this practically excludes most of the so far used transition metals or metal oxides. Therefore our research goal is the synthesis of nanostructured organic materials from abundant precursors using self-assembly, templating or nanocasting techniques and their application as catalysts, electrode materials, gas storage devices, membranes and separation media.

Carbon

The search for new synthetic strategies for generating nanostructured carbon or carbon-hybrid materials is an exciting topic in material chemistry, motivated by the natural abundance and therefore cost-efficiency of carbon precursors and on the other hand promising applications of the resulting materials. The synthesis of carbon materials, as performed today, always relies on very harsh conditions (e.g. pyrolysis), which makes modifications of the surface functionality especially difficult. In contrast we use a mild hydrothermal route to produce µm-sized, colloidal carbon spheres, distinguished by a hydrophilic surface of the particles (**see Fig. 1a**) **[1]**. The resulting carbon structures can be further controlled when suitable templates are introduced in the synthesis. Hydrothermal carbonization for instance can be carried out in the pores of porous silica beads yielding porous carbon spheres with a hydrophilic surface area (**see Fig. 1b**) **[2]**. These carbon spheres can act as templates on their own and were successfully used for the direct synthesis of metal oxide hollow spheres by addition of metal salts into the hydrothermal reaction mixture **[3]**.

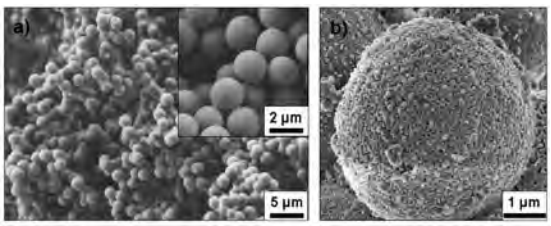


Fig. 1: Hydrothermal carbonisation of carbohydrates: a) direct production of colloidal carbon spheres b) mesoporous carbon particles via hydrothermal carbonization inside porous silica beads

Carbon Nitrides

Many of today's catalytic systems are not sustainable solutions, because they are based on rare elements (e.g. noble metals). Therefore the replacement of these materials by catalysts derived from abundant elements or, as the most elegant possibility, a "metal-free" catalyst is a valuable object for future catalyst research. Such a catalyst is provided by graphitic carbon nitride, g-C_3N_4. Graphitic Carbon Nitride (g-C_3N_4) is a material, which is easily obtained through thermal condensation of cyanamide, dicyandiamide or melamine. Following a reaction/condensation scheme the resulting materials adopt a very special architecture, with a graphitic stacking and individual layers composed of condensed melem units, yielding a material which combines lewis-acidicity with interesting electronic properties. A mesoporous graphitic C_3N_4 (mpg-C_3N_4) can be produced using colloidal silica particles as templates (**see Fig. 2**) **[4]**.

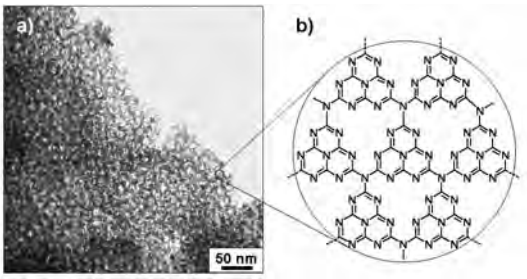


Fig. 2: a) TEM-micrograph and b) chemical structure of the pore walls of mesoporous graphitic carbon nitride (mpg-C_3N_4)

Mesoporous graphitic carbon nitride was shown to be a versatile heterogeneous, metal-free catalyst for the Friedel-Crafts acylation of benzene, which proceeds via the activation of the aromatic ring **[4,5]**, the cyclotrimerizations of substituted nitriles and alkynes **[6]** and for an unusual activation of CO_2 **[7]**.

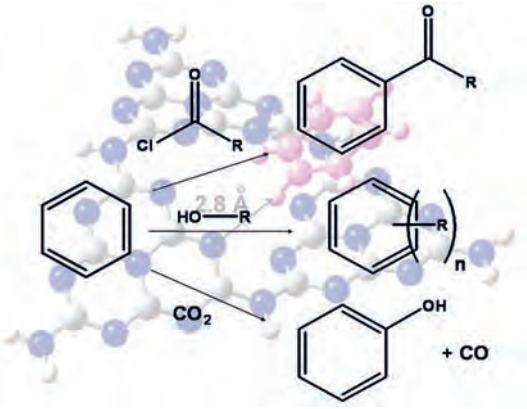


Fig. 3: Chemical reactions with benzene catalyzed by mpg C_3N_4

References:
[1] Wang, Q., Li, H., Chen, L.Q., Huang, X.J.: Monodispersed hard carbon spherules with uniform nanopores. Carbon **39**, 2211-2214 (2001)
[2] Titirici, M.M., Antonietti, M., Thomas, A.: Replication and Coating of Silica Templates by Hydrothermal Carbonisation. Adv. Funct. Mater. 17, 1010-1018, (2007)
[3] Titirici, M.M., Antonietti, M., Thomas, A.: A Generalized Synthesis of Metal Oxide Hollow Spheres Using a Hydrothermal Approach Chem. Mater. **18**, 3808-3812 (2006).
[4] Goettmann, F., Fischer, A., Antonietti, M., Thomas, A.: Chemical Synthesis of Mesoporous Carbon Nitrides Using Hard Templates and Their Use as a Metal-Free Catalyst for Friedel-Crafts Reaction of Benzene. Angew. Chem. Int. Ed. 45, 4467-4471 (2006).
[5] Goettmann, F., Fischer, A., Antonietti, M., Thomas, A.: Metal free catalysis of sustainable Friedel-Crafts reactions: Direct activation of benzene by carbon nitrides to avoid the use of metal chlorides and halogenated compounds. ChemComm. **43**, 4530-4532 (2006).

In another application, mpg-C_3N_4 can be used as a nanoreactor for the preparation of metal nitride nanoparticles. In this approach the carbon nitride acts, firstly as a confinement for nascent nanoparticles and then, during decomposition, as a nitrogen source, generating metal nitride nanoparticles of various compositions **[8]**.

Polymers

Poly(benzimidazole) (PBI) has a good proton conductivity in a wide temperature window when doped with acids. PBI has therefore high potential for applications in proton exchange membrane fuel cells (PEMFCs). New nanostructured polymer membranes based on poly(benzimidazole) with enhanced properties in terms of conductivity and thermal stability were synthesized by a casting approach via a monomer adsorption/polycondensation process inside the pores of selected mesoporous silicas **[9]** or using colloidal silica as templates (**see Fig. 4**) **[10]**.

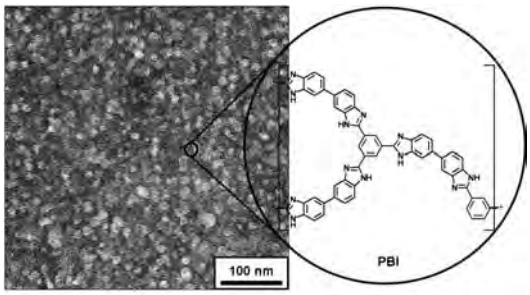


Fig. 4: TEM picture and chemical structure of a mesoporous poly(benzimidazole)

The porosity and surface area of the resulting mesoporous polymers can be tuned by the amount of the silica template but also by varying the cross-linking density of the polymer frameworks. The so obtained mesoporous PBIs show improved proton conductivity at temperatures above 100°C when doped with phosphoric acid **[11]**.

Organosilicas

Mesoporous organosilicas (MOs) represent a promising class of organic-inorganic nanocomposites because they combine the unique features of porous glasses, such as high surface areas and defined pore structures, with the chemical functionality and physical properties of organic materials Their distinct feature is the presence of organic groups incorporated into the channel walls of a mesoporous structure.

We introduced an "all-in-one approach" controlling functionality and porosity of organosilicas by using a specially designed monomer, combining the features of a surfactant and a silica precursor (**see Fig. 5**) **[12]**.

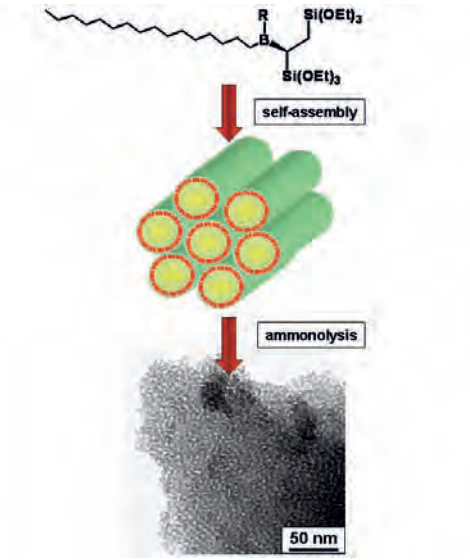


Fig. 5: All-in-one approach for the synthesis of functional mesoporous materials

These monomers self-organize when hydrolysis of their inorganic part takes place via an aggregation of their organic parts into hydrophobic domains. Porous materials are made from these monomers via a condensation/ammonolysis sequence, while the monomer architecture ensures an exclusive arrangement of functional groups along the channel interfaces. Recently this approach was extended to the preparation of chiral mesoporous organosilicas **[13]**.

A. Thomas, M. Bojdys, R. D. Cakan, A. Fischer, F. Goettmann, A. Ide, P. Kuhn, P. Makowski, F. Roohi, M. M. Titirici, J. Weber, M. Antonietti
arne.thomas@mpikg.mpg.de

[6] Goettmann, F., Fischer, A., Antonietti, M., Thomas, A.: Mesoporous graphitic carbon nitride as a versatile, metal free catalyst for the cyclisation of functional nitriles and alkynes. submitted
[7] Goettmann, F., Thomas, A., Antonietti, M.: Metal-free Activation of CO_2 by Mesoporous Graphitic Carbon Nitride. Angew. Chem. Int. Ed. **46**, 2717-2720, (2007)
[8] Fischer, A., Antonietti, M., Thomas, A.:Growth Confined by the Nitrogen Source: Synthesis of Pure Metal Nitride Nanoparticles in Mesoporous Graphitic Carbon Nitride. Adv. Mater. **19**, 264-267, (2007)
[9] Groenewolt, M., Thomas, A., Antonietti, M.: Nanoparticles and nanosheets of aromatic polyimides via polycondensation in controlled pore geometries. Macromolecules **37**, 4360-4364 (2004).
[10] Weber, J., Antonietti, M., Thomas, A.: Mesoporous Poly(benzimidazole) Networks via Solvent Mediated Templating of Hard Spheres Macromolecules 40, 1299-1304, (2007)
[11] Weber, J., Maier, J., Antonietti, M., Thomas, A. in preparation
[12] Voss, R., Thomas, A., Antonietti, M., Ozin, G.A., Synthesis and Characterization of Highly Amine Functionalized Organosilicas by an "All-in-One" Approach. J. Mater. Chem. **15**, 4010-4014 (2005).
[13] Ide, A., Voss, R., Scholz, G., Ozin, GA., Antonietti, M., Thomas, A.: Organosilicas with Chiral Bridges and Self-Generating Mesoporosity. Chem. Mater. **19**, 2649-2657, (2007)

Synthesis and Characterization of Self-assembled Inorganic Materials

Bernd Smarsly 21.12.1971
1998: Diploma, Physical Chemistry (University of Marburg, Germany)
Thesis: Structure investigations of phenylalkyl-substituted poly-(p-xylylene)s
2001: PhD, Physical Chemistry (University Potsdam)
Thesis: Characterization of porous materials by small-angle scattering techniques
2002-2003: Postdoc (University of New Mexico, Albuquerque, USA)
Since 2003: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Various "classical" inorganics are supposed to possess advanced properties if scaled down to the nanometer region. If prepared in the form of materials with pores on the nanometer scale ("mesopores", pore size 3-50 nm), especially carbonaceous materials and metal oxides offer attractive fields of applications requiring strong interaction with other molecules or ions, e.g. in catalysis, sensing, chromatographie and electrochemical processes. Meanwhile, different sol-gel strategies, based on self-assembly of surfactants, are known to obtain such materials in form of powders. However, a lot of devices require crack-free thin coatings of such mesoporous metal oxides. Our research in this project is dedicated to the generation of such mesoporous layers and also the development of suitable characterization methods (pore size, pore shape and arrangement, etc.). Finally, we aim to understand if the porosity and downscaling to nanometer-sized crystals indeed results in better physico-chemical properties, e.g. in terms of the sensibility of sensing, storage of electric energy, etc. Recently, we described a general methodology for the generation of diverse metal oxides as homogeneous coatings with highly ordered 3D mesopores of ca. 14 nm in diameter, taking advantage of evaporation-induced self-assembly in combination with novel types of block copolymers **[1]**. Such films usually have to be prepared in the crystalline modification, because the physico-chemical functionality (sensing, catalysis, etc.) is only exhibited by a highly crystalline oxidic matrix. Here we present exemplarily mesoporous WO_3 (tungsten oxide) films, which is industrially used for the coloration of glass. WO_3 is an ideal model system, because it exhibits a reversible color change (transparent-blue) upon reversible electrochemical reduction/oxidation between W(VI) and W(V) and insertion/desertion of Li^+ or H^+ ions, respectively. These color changes can be easily detected and quantified in terms of the coloration efficiency, the switching time, etc., and related to the porosity and crystallinity of the material. Since current devices based on dense, non-porous WO_3-coatings (e.g. WO_3-covered rear-back mirrors) suffer from relatively slow (de)coloration times, a highly mesoporous, crystalline WO_3 film should theoretically show improved performance owing to the facilitated diffusion of the electrolyte in and out the WO_3 film through the pores. The well-defined mesostructure is well seen by microscopic techniques (**Fig. 1**), revealing arrays of almost monodisperse spherical mesopores, which are slightly deformed. The films have a thickness between ca. 100 and 1000 nm. However, microscopic techniques inevitably present only local information about the structural order. To test the overall quality of the mesostructure over larger areas, we have developed special small-angle x-ray scattering (SAXS) techniques to study the mesostructure in such thin film. In essence, the films are prepared on ultrathin Si wafers, which can be penetrated by x-ray beams. Using our in-house rotating anode setup, equipped with a specially designed sample-holder and a 2D area detector, even thin films of only 100 nm in thickness can be investigated. **Fig. 2** shows typical 2D SAXS patterns of mesoporous WO_3 films. SAXS analyses reveal that these patterns are attributable to a body-centered cubic (BCC) packing of 14 nm spherical pores with a pore-to-pore distance of ca. 22 nm.

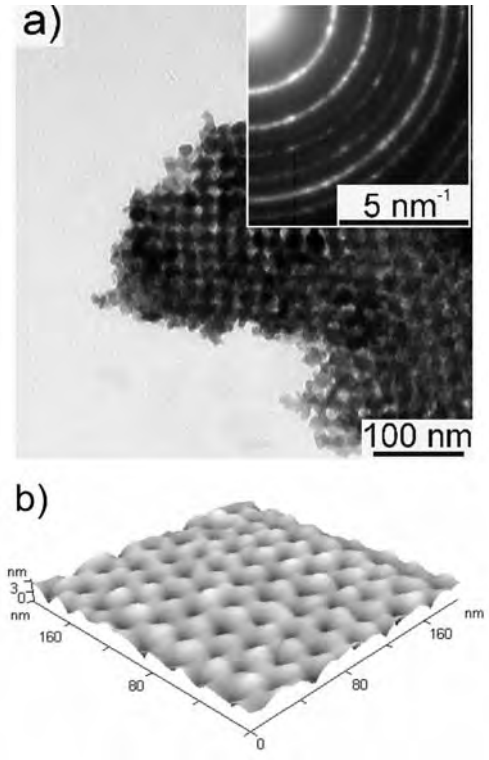


Fig. 1: Microscopic characterization of WO_3 films.
a) Transmission Electron Microscopy and electron diffraction (inset) of.
b) Atomic Force microscopy (tapping mode).

Since the X-ray beam can be scanned over the specimen, such experiments allow to study the macroscopic homogeneity of thin mesostructured coatings. Also, only 2D SAXS measurements allowed to determined the orientation of the mesostructure. In contrast to powder materials, mesostructured films often exhibit a preferred orientation of the mesostructure relative to the substrate, in this case a [110] orientation of the BCC mesopore arangement

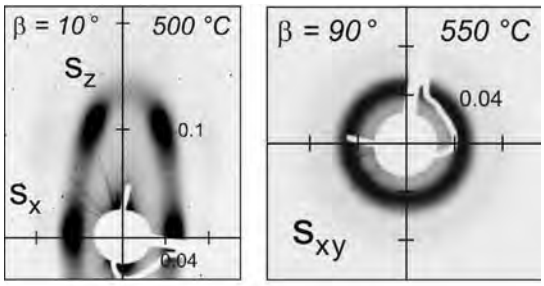


Fig. 2: 2D-SAXS patterns of WO_3 films treated at high temperature (to induce crystallization) as a function of the angle of incidence , between the x-ray beam and the film surface. The scattering vector s is given in units of nm^{-1}.

In order to understand, if such mesoporous, crystalline films indeed show improved physico-chemical performance, the coloration behaviour of WO_3 films was studied during the electrochemical oxidation/reduction process. As a suitable criterion, we used the "coloration efficiency" η, which basically describes a measure for the color depth (blue) per applied charge. η was determined as a function of the porosity and degree of crystallinity. Since usually windows may be exposed to varying temperatures (sun-light), also the operation temperature was varied. Such experiments (**Fig. 3**) reveal interesting trends regarding the influence of the structural parameters (porosity, crystallinity). First, mesoporous WO_3 films show a significantly faster coloration switching response between blue and transparent state on the order of several seconds only (not shown), owing to the better accessibility of the WO_3 nanocrystals, which is ca. 3 times faster than non-porous films. Second, the coloration behaviour itself is substantially influenced by the state of WO_3. We found that only mesoporous WO_3 films with a high degree of crystallinity showed good electrochemical stability and coloration efficiency, while mesoporous films with an amorphous or only partially crystalline matrix lack sufficient stability upon long-term treatment and exposure to higher temperatures, i.e. harsh environmental conditions. Furthermore, also the absolute values of the coloration efficiency were good taking into account the relatively low film thickness. In conclusion, these experiments demonstrated that mesoporous films of metal oxides indeed show improved electrochemical properties. Similar results were obtained for other mesoporous metal oxide films (TiO_2, ITO) **[3]**.

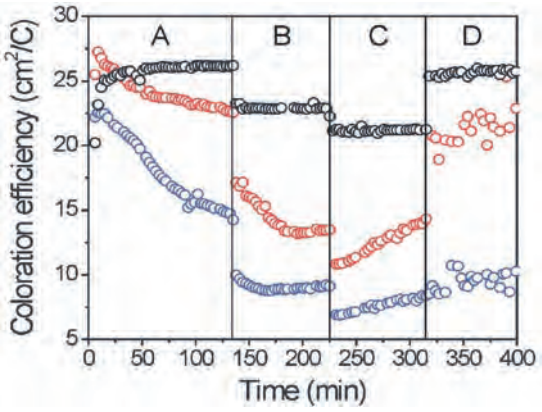


Fig. 3: Coloration efficiency of mesoporous WO_3 thin films with varying degrees of crystallinity (tuned by different heat-treatment temperatures) as a function of the operating temperature. The notation of films is as follows: amorphous (blue circuits), partially crystalline (red circuits), and fully crystalline (black circuits). A, B, C and D correspond to the following operating temperatures: 20 °C, 50 °C,70 °C and 20 °C (after cooling from 70 °C).

B. Smarsly, M. Antonietti, Philipp Adelhelm, Torsten Brezesinski, Laemthong Chuenchom, Helena Kaper, Regina Rothe, Sébastien Sallard, Özlem Sel, Wu Jin-Ming, Wang Yude
bernd.smarsly@mpikg.mpg.de

References:

[1] Smarsly, B., Antonietti, M.: Block copolymer assemblies as templates for the generation of mesoporous inorganic materials and crystalline films. Europ. J. Inorg. Chem. 1111-1119 (2006).

[2] Brezesinski, T., Fattakhova-Rohlfing, D., Sallard, S., Antonietti, M., Smarsly, B. M.: Highly crystalline WO_3 thin films with ordered 3D mesoporosity and improved electrochromic performance. Small **2**, 1203 – 1211 (2006).

[3] Fattakhova-Rohlfing, D., Brezesinski, T., Rathouský, J., Feldhoff, A., Oekermann, T., Wark, M., Smarsly, B.: Transparent Conducting Films of Indium Tin Oxide with 3D Mesopore Architecture Adv. Mater. **18**, 2980–2983 (2006).

Fractionating Colloid Analytics

Helmut Cölfen 24.07.1965
1991: Diploma, Physical Chemistry (University of Duisburg)
Thesis: Analytical Ultracentrifugation of Gels
1993: PhD, Physical Chemistry (University of Duisburg)
Thesis: Analytical Ultracentrifugation of Gels
1993-1995: Postdoc (National Center 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
Since 2004: Private Docent; University of Potsdam

Analytical Ultracentrifugation (AUC) and Field-Flow fractionation (FFF) are powerful fractionating analysis methods for colloids and polymers. AUC is available as an active service unit for a large variety of colloid and polymer analysis problems from the institute and external cooperation partners **[1-4]**. We have three main working directions in this project: a) detector development b) method development c) colloid and polymer characterization. For the latter, special emphasis was laid on complex polymer and supramolecular systems as well as polymer-inorganic hybrid particles, which are very difficult to characterize by other analytical methods. One example is Zn metallosupramolecular architectures, where AUC could prove the molecular integrity of the defined and monodisperse metallosupramolecular complex in solution **[1]**.

A second generation dendronized polymer resulting from free radical polymerization of the macromonomer could also successfully be characterized in terms of molar mass and polydispersity as an example for polydisperse polymers with a very high molar mass > 10^6 g/mol **[2]**. The results were found in good agreement with those from other analytical techniques but AUC could yield a distribution instead of average values from other techniques like light scattering.

AUC is a versatile analytical technique, which can be applied to many more analytical questions than the traditional molar mass or sedimentation coefficient distribution. For the example of microgels containing partially uncrosslinked material, the amount of each component can be quantitatively determined **[3]**. However, the sedimentation coefficients depend on friction and a sedimenting swollen microgel has a higher friction and thus lower sedimentation coefficient compared to the unswollen microgel. Therefore, the swelling degree can be calculated from the sedimentation coefficients of swollen and non-swollen samples. Determining the sedimentation coefficient distribution of swollen and deswollen microgels for the first time enabled the determination of a swelling degree distribution as shown in **Fig. 1**. Despite some instability of the evaluation at the highest swelling degree of the weakly cross-linked microgel, the swelling degree distributions allow for a detailed analysis of the homogeneity of cross-linking, which is expressed in a narrow swelling degree distribution.

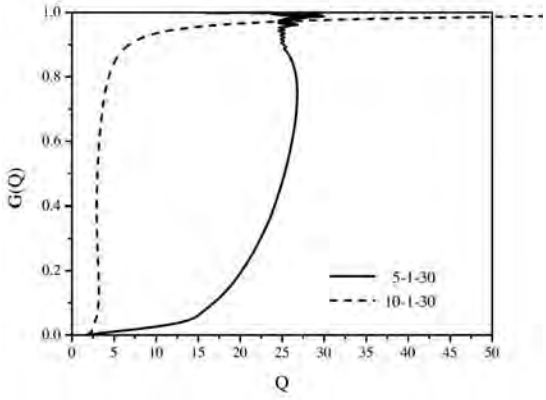


Fig. 1: Integral volume degree of swelling distributions evaluated from sedimentation coefficient distributions in the collapsed and swollen state for a highly crosslinked (10-1-30) and weakly crosslinked (5-1-30) microgel of poly(N-isopropylacrylamide) (NIPAAm).

However, in the present example, it can be seen that the highly cross-linked microgel (10-1-30) has a tailing towards higher swelling degrees meaning that ca. 5% of the microgels are more weakly crosslinked. In turn, the weakly crosslinked microgel has a similar fraction of more cross-linked microgels.

The integrity of organic-inorganic hybrid particles can also advantageously be investigated by AUC. In case of DNA coated hydroxyapatite, which was synthesized in several layers for gene transfection applications, the formation of DNA resp. hydroxyapatite shells could be shown directly in solution and the integrity of the nanoparticles was demonstrated **[4]**. This is another application taking advantage of the fractionating capability of an AUC to detect all components present in a complex mixture.

Another focus of our work was the development of new experimental methods for AUC. By sedimentation of a polyacid like poly(styrene sulfonate) under salt free conditions, a pH gradient spanning a few units of pH can be built up in the AUC cell. If charged particles are sedimented in such gradient, information about their charge or aggregation behaviour can be deduced as was demonstrated for gold colloids with different charge **[5]**.

If hybrid colloids or very small colloids are investigated by AUC, the determination of the particle density is often problematic, as the samples can exhibit a density distribution. This could in principle be accessed by density gradient ultracentrifugation for densities up to 2 g/ml. However, particle stability issues hinder the application of salts and organic solvent mixtures endanger preferential solvation problems. Application of the density variation method running experiments in H_2O and D_2O combining the respective sedimentation coefficient distributions can circumvent this problem and can yield density distributions with a quite robust determination of the particle density **[6]**. This method appears promising for the analysis of hybrid organic-inorganic as well as nanoparticles with higher density by AUC.

The improvement of the AUC detection systems is of great importance for colloid analysis by AUC to derive more information on the fractionated samples. We have therefore continued our development of a UV-Vis multiwavelength detector as well as Raman and small angle laser light scattering detector in cooperation with the BASF AG.

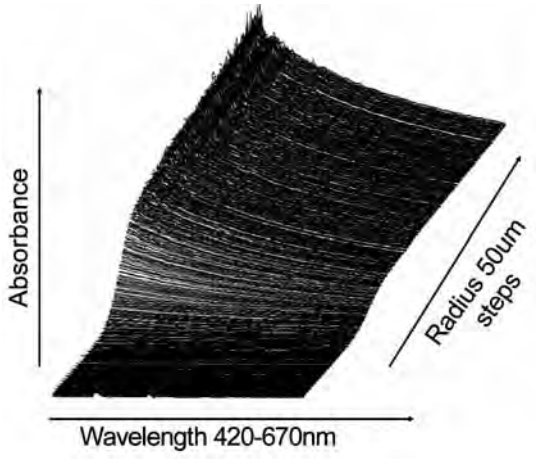


Fig. 2: Radial Scan for a 175 nm polystyrene latex sample (10000rpm, 25°C).

The UV-Vis multiwavelength detector could be advanced to a prototype stadium including hard- and software development and the quality of the experimental results be improved **[7]**. The detector has two main advantages: Speed and simultaneous detection of a whole UV-Vis spectrum instead of a single wavelength as in all previous analytical ultracentrifuges. This is shown in **Fig. 2**. The additional spectral information allows for example for multiple sensitivity in the investigation of colloid particle size distributions as the turbidity is wavelength dependent. Therefore, small colloids can advantageously be investigated at smaller wavelengths, bigger colloids at a higher wavelength, which is advantageous if particles with very broad particle size distributions or multicomponent mixtures are to be investigated. Multiple wavelength detection is also useful to average information over several wavelengths to improve the signal to noise ratio or to investigate complex mixtures with multiple chromophores. Generally, the increase in the data space by a further dimension increases the information content of an experimental scan very much.

The detector also allows for the application of a speed profile with a fixed detector position, where all particles pass the detector at a defined speed. This is useful if unknown samples or samples with very broad sedimentation coefficient distributions are to be investigated.

Another detection system which is improved is the Rayleigh interference optics, which is currently installed on the commercial instrument. Application of a larger camera as detector as well as of a new laser mount should significantly improve the data quality of this optical system as more data are captured and the light source is mechanically decoupled. We hope that improvement of this detector together with the multiwavelength detector will enable faster measurements with much more information content than present to date on a routine basis. This is important to enable the investigations of increasingly complex colloidal systems.

H. Cölfen, A. Völkel, S.K. Bhattacharyya, A.M. Gülsün, H.B. Cicek, M. Strickhausen, H. Strauss
Coelfen@mpikg.mpg.de

References:

[1] Schmittel, M., Kalsani, V., Kishore, R. S. K., Cölfen, H. and Bats, J. W. Dynamic and Fluores-cent Nanoscale Phenanthroline/Terpyridine Zinc(II) Ladders. Self-Recognition in Unlike Ligand/Like Metal Coordination Scenarios. J. Amer. Chem. Soc. **127**, 11544-11545 (2005).

[2] Kasemi, E.; Zhuang, W.; Rabe, J. P.; Fischer, K.; Schmidt, M.; Colussi, M.; Keul, H.; Yi, D.; Cölfen, H. and Schlüter, A. D., Synthesis of an anionically chargeable, high-molar-mass, second-generation dendronized polymer and the observation of branching by scanning force microscopy. J. Amer. Chem. Soc. **128**, 5091-9 (2006).

[3] Kuckling, D., Vo, C. D., Adler, H. J. P., Völkel, A. and Cölfen, H. Preparation and Characterization of Photo-Cross-Linked Thermosensitive PNIPAAm Nanogels. Macromolecules **39**, 1585-1591 (2006).

[4] Sokolova, V.; Prymak, O.; Meyer-Zaika, W.; Cölfen, H.; Rehage, H.; Shukla, A. and Epple, M. Synthesis and characterization of DNA-functionalized calcium phosphate nanoparticles. Materialwissenschaft und Werkstofftechnik **37**, 441-445 (2006).

[5] Cölfen, H. and Lucas, G. Particle sedimentation in pH-gradients. Progr. Colloid Polym. Sci. **131**, 129-133 (2006).

[6] Cölfen, H. and Völkel, A. Application of the density variation method on calcium carbonate nanoparticles. Progr. Colloid Polym. Sci. **131**, 126-128 (2006).

[7] Bhattacharyya, S. K.; Maciejewska, P.; Börger, L.; Stadler, M.; Gülsün, A. M.; Cicek, H. B. and Cölfen, H. Development of a fast fiber based UV-Vis multiwavelength detector for an ultracentrifuge. Progr. Colloid Polym. Sci. **131**, 9-22 (2006).

Electron Microscopic Studies of Colloidal Systems and Biomaterials

Jürgen Hartmann 18.10.1953
1977: Diploma, Physics
(Humboldt University Berlin; Institute of Low-Temperature Solid State Physics)
Thesis: Application of Square-Wave Polarography and a Density Method for the Analysis of Bismuth-Antimon Alloys
1977–1991: Research Scientist
(Institute for Polymer Chemistry, Teltow)
1987: PhD, Polymer Physics
(Institute of Polymer Chemistry, Teltow)
Thesis: Contribution to the Formation Mechanism of Coagulation Structures of Polymers Using Electron Microscopy
1992–1995: Research Scientist
(Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 1995: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

Transmission, high-resolution scanning and environmental electron microscopy are suitable tools to investigate the morphological structure of polymer micelles and particles, organic and inorganic crystals and nanoparticles, aggregates of biopolymers, poly-electrolyte complex shells, composite materials and naturally-grown biomaterials. The determination of structural parameters like the size and size distribution of colloidal particle systems, the pore size of polymeric and inorganic networks, the spatial arrangement of crystallites and the determination of crystal structures are the main aspects of our electron microscopic research. Because of the organization of the institute, there is a close cooperation with a number of research groups of the colloid chemistry, interface and biomaterials departments. Some of the interesting results are presented here.

An especially fascinating class of crystals are colloidal crystals with non-spherical and perfectly-aligned building blocks. The crystallization of organic molecules, e.g. amino acids, controlled by double hydrophilic block copolymers (DHBC's) such as poly(ethylene glycol)$_{3000}$-((L-Glutamic Acid)-(L-Glutamic Acid)-(L-Serine))$_{1100}$ (PEG-EES) are suitable for studying the nanoparticle formation of DL-alanine and their self-assembly and subsequent mesoscopic transformation to core-shell and hollow alanine rods.

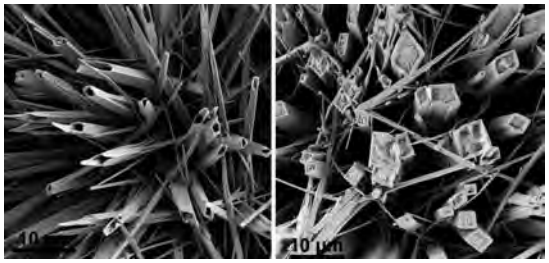


Fig. 1: DL-alanine tubes formed under supersaturated conditions in the presence of 3.3 gL^{-1} of PEG-EES (left) and of 0.67 gL^{-1} PEG-EES (right) at room temperature.

Whereas the normal crystallization of DL-alanine from a supersaturated solution in the absence of additives results in compact needle-like crystals, the use of PEG–peptide conjugate as a crystal growth modifier generates elongated DL-alanine crystals with tubular characteristics (**Fig.1**). The main axis is longer than 50 µm, the tubes have diameters of about 1-2 µm and the wall thickness is in the range of 80-120 nm. Some of the crystals have square cross-sections. At lower PEG-EES concentrations, the rate of crystallization of DL-alanine and the number of crystals are decreased and the diameters of the aggregated nanoparticles are about 200 nm and they are located inside the tubes (**Fig. 1**). The edge lengths of the core-shell structure are in the range of 2-4 µm and the maximum length of the tubes is longer than 100 µm. The tube-like crystals illustrates the morphology control provided by the DHBC.

A different type of solidification is the crystallization of microdroplets consisting of amino acids and oppositely charged polyelectrolytes in ethanol/water mixtures. For the basic amino acids L-lysine and L-histidine, polyacrylic acid (Mw = 2000 g mol^{-1}) is used as a cationic polyelectrolyte. To promote the crystallization, the amino acid concentration has to be increased up to 10 wt%. The diameters of the grown spherical crystalline superstructures are in the range of 10-100 µm. The more or less radially-aligned smaller platelet-like crystals with a diameter of few microns and a thickness of around 30 nm are forming spheres of high inner surfaces (**Fig. 2**). L-lysine usually forms compact, irregular, elongated crystals with a size of 50 to 400 µm. The thin platelet-like crystal growth indicates the morphology control provided by the cationic polyelectrolyte.

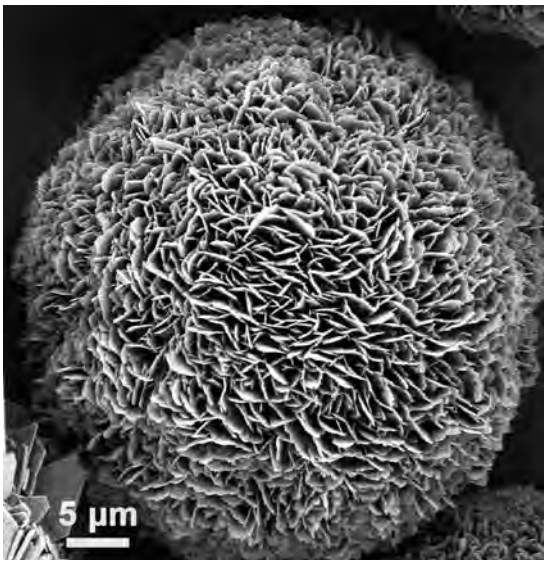


Fig. 2: L-lysine crystal superstructures.

One of the main projects is the electron microscopic investigation of gold-patterned, spherical, colloidal, particles. Using the upper single or double layers of colloidal crystals as masks during gold vapour deposition, various gold patterns were successfully produced on the surfaces of the spheres in lower regions (**Fig. 3**). The gold atoms reach the spheres in the second layer only through interstices between the top layer spheres. The dimension and geometry of the generated gold patterns depends on the particle size, the structure of the colloidal crystal templates, the number of upper layers, and the time of plasma etching.

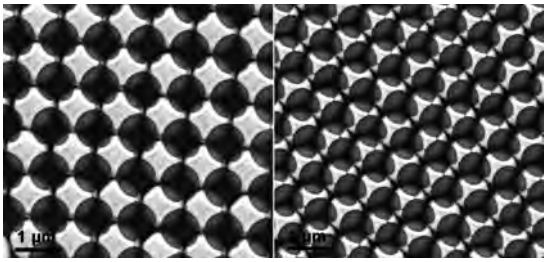


Fig. 3: Gold-patterned polystyrene (PS) particle sur-faces generated by templating the top monolayers of colloidal crystals with preferential crystal orientation of (100) (left) and gold-coated PS colloidal crystals, etched by O_2 - plasma for 10 min. The preferential orientation of the crystal is (111) parallel to the sub-strate (right).

An interesting example for the combination of electron microscopy and elemental analysis is the control of the preparation of hierarchical molecular imprinting of polymer (MIP) materials. After immobilisation of target molecules on the surface of a mesoporous inorganic substrate, followed by a complete pore filling appropriate monomer mixture, subsequent polymerisation and removal of the inorganic support the final MIP material is produced. To investigate the internal structures an effective embedding technique for ultra-thin sectioning of the composite materials was developed. The structure of the mesoporous silica precursor and imprinted polymer composite and the pure imprinted polymer material is shown in **Fig. 4**.

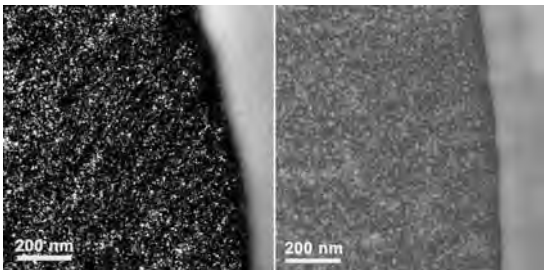


Fig. 4: Ultra-thin section of the porous silica template (left) in the presence of the hierarchical imprinted polymer of the dipeptide sequence H-phenylalanine-glycin-Si and the pure imprinted polymer material after removal of the silica matrix (right).

The electron microscopic investigations indicate that the porosity of the replicated polymeric material is of the same order of magnitude as in the silica template.

The success of the imprinting process is also checked by measuring the carbon content of the silica precursor/imprinted polymer composite and the determination of the silica content of the imprinted polymers after removal of the silica template by treatment with aqueous solution of NH_4HF_2 by EDX spectroscopy (**Fig. 5**).

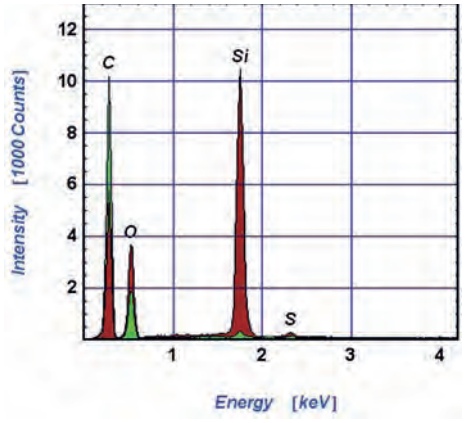


Fig. 5: EDX spectra of the silica/polymer composite (brown curve) and of the imprinted polymer material (green curve).

Another example of the formation of hierarchical structured materials is the inorganic nanoparticle casting of wood, which is well suited as a template. The cell-wall layers consist of parallel arrays of cellulose fibrils embedded in a matrix of hemicelluloses and lignin. To obtain cellulose/nanoparticle composites $Ce_{0.5}Zr_{0.5}O_2$, nanoparticle sols (particle diameter $\approx$ 1.5 nm) were incorporated into the native tissue. After drying and slow calcination at 500°C, mechanically stable, pure, inorganic materials were formed. It is shown in **Fig. 6** that the templating occurs at the level of the cellulose microfibrils and not at the level of the fibril aggregates.

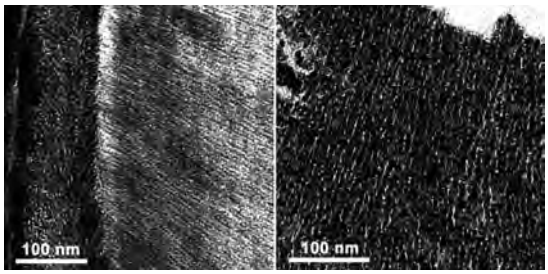


Fig. 6: Ultra-thin cross section of impregnated and dried compression wood tissue (left) and after calcination (right)

The spacing between the dark filaments representing the inorganic nanoparticles for the impregnated sample is around 2-4 nm which is consistent with the diameter of cellulose fibrils, and is about double sized in the calcined sample. After calcination the nanoparticles are partly coalesced and sintered together, but they represent the typical fibrillar structure of the cellulose.

In the future, more detailed electron microscopic investigations of the spatial distribution of inorganic compounds in hierarchically structured biomaterials are of special interest.

J. Hartmann, H. Cölfen, H.G. Börner, S. Wohlrab, M.M. Titirici, D. Wang, O. Paris, H.S. Gupta, I. Burgert, A. Deshpande
juergen.hartmann@mpikg.mpg.de

References:

[1] van Maanen, G. J., Seeley, S. L., Hartmann, J., Bukovnik, R., Spontak, R. J.: Property and Morphology Development in Nano-composite Thermoplastic Elastomer Gels. Langmuir, **21**(7):3106-3115 (2005).

[2] Khopade, A.J., Arulsudar, N., Khopade, S.A., Hartmann, J.: Ultrathin Antibiotic Walled thin Microcapsules. Biomacromolecules, **6**(1), 229-234 (2005).

[3] Kuang, M., Wang, D., Gao, M., Hartmann, J., Möhwald, H.: A Bio-inspired Route to Fabricate Submicrometer-Sized Particles with Unusual Shapes - Mineralization of Calcium Carbonate within Hydrogel Spheres. Chem. Mater. **17**, 656-660 (2005).

[4] Zhang, G., Wang, D., Gu, Z., Hartmann, J., Möhwald, H.:Two-Dimensional Non-Close-Packing Arrays Derived from Self-Assembly of Biomineralized Hydrogel Spheres and Their Patterning Applications. Chem. Mater. **17**, 5268-5274 (2005).

[5] Gupta, H. S., Wagermaier, W., Zickler, G. A., Hartmann, J., Funari, S. S., Roschger, P., Wagner, H. D. & Fratzl, P.: Fibrillar Level Fracture in Bone Beyond the Yield Point. International Journal of Fracture (2006) **139**, 425-436 (2006).

[6] Ma,Y., Börner, H., Hartmann, J., Cölfen, H.: Synthesis of DL-alanine hollow tubes and core-shell mesostructures. (Accepted Cem. Eur. J. 2006)

[7] Polarz, S., Regenspurger, R., Hartmann, J.:Hierarchical Self-Assembly of organometallic Zinc-Poly(ethylene glycol) Hybrids.(Submitted to Macromol. Rapid Comm.).

Light Scattering at Interfaces

Reinhard Sigel 14.03.1965
1992: Diploma, Physics
(Albert-Ludwigs-Universität Freiburg)
Thesis: Stress Optical Behaviour of Liquid Crystalline Elastomers
1997: PhD, Physics
(Albert-Ludwig University of Freiburg)
Thesis: Investigation of the Nematic Wetting Layer in an Isotropic Liquid Crystal by Evanescent Wave Light Scattering
1997-1998: Postdoc
(Albert-Ludwig University of Freiburg)
1998-2000: Postdoc
(Institute of Electronic Structure and Laser, Heraklion, Crete, Greece)
Since 2000: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

Soft interfacial structures are of high interest because of their ability to react on an external excitation. Abundant examples are found in biological interfaces. Life relies on function of the constituting structures, and this function is induced by a suitable stimulus. Target of research are such soft structures at interfaces, especially the spherical interfaces of dispersed colloidal particles and planar liquid-air or liquid-liquid interfaces. Intrinsically tied to soft degrees of freedom are fluctuations. They can be used for the detection of softness and, correspondingly, of function. For bulk samples, light scattering is a well established tool to detect fluctuations. The team focuses on the development and the application of interface sensitive light scattering techniques for the characterization of soft, functional interfaces.

Colloidal Interfaces

Ellipsometric light scattering is a technique developed in our group for the characterization of thin interfacial layers on dispersed colloidal particles **[1]**. Its working principle is similar to classical reflection ellipsometry, where the reflection at the planar interface is replaced by a scattering process. Data evaluation is based on Mie scattering theory.

As an application, the salt concentration around charged stabilized colloids was investigated **[2]**. Unexpectedly, there is a transition from a low salt concentration compatible with a Poisson-Boltzmann description to a rather high concentration within a layer around the colloidal particles. This sudden transition at a defined average salt concentration has been identified as a first order pre-wetting transition at the colloidal particles interface.

Vesicles composed of DPPC (1,2-Dipalmitoyl-sn-glycero-3-phosphocholine) are anisotropic spherical shells. The two parameters of ellipsometric light scattering, tan(Ψ) and Δ, show a high sensitivity on this anisotropy, as displayed in **Fig. 1**. While for isotropic shells the minimum of tan(Ψ) and the step in Δ is expected at a scattering angle Θ larger than 90°, they are found below 90° for the anisotropic vesicles. The quantitative evaluation of these data yields an order parameter S=0.71 within the vesicle shell **[3]**, corresponding to an average tilt angle β larger than 29°. This lower limit fits well to the value β=32° found in planar DPPC-layers. Packing arguments confirm, that the effect of the layer bending in the vesicles is negligible for this rather low curvature.

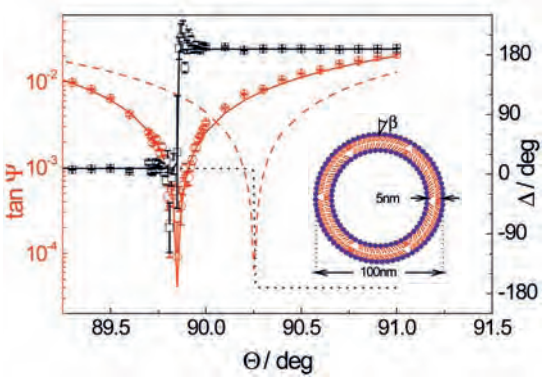


Fig. 1: Ellipsometric data tan(Ψ) (red) and Δ (black) versus the scattering angle Θ for DPPC vesicles). The broken lines mark the expected behaviour of a vesicle with an isotropic shell. The inset shows a sketch of a vesicle with an anisotropic shell.

As an experimental improvement, a new apparatus for spectroscopic elliposmetric light scattering was built up. Measurements at several wavelengths of light are expected to yield a substantial increase in resolution. The usage of a camera as a two dimensional detector drastically speeds up the measurements, so multi wavelength measurements are feasible in a reasonable amount of time. First data on charge stabilized colloidal of 100nm radius are shown in **Fig. 2**. There is a characteristic evolution of the position and the depth of the minimum of tan(Ψ). In parallel, the position and the slope of the step in Δ change. While at large wavelength the step goes from Δ=0° to Δ= -180°, it is reversed to a step Δ=0° to Δ=180° at short wavelengths. The wavelength where the transition of the step direction occurs is highly sensitive on the thickness of a layer on the colloidal particles. Its detection is the basis of the improvement in resolution.

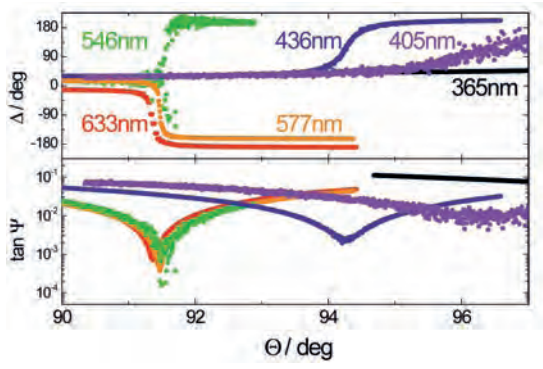


Fig. 2: Ellipsometric parameters Δ and tan(Ψ) versus the scattering angle Θ for several wavelengths of light (as indicated in the plot).

Fluctuations at Planar Liquid-Fluid Interfaces

Fluctuations close to a planar interface can be accessed by light scattering with an evanescent wave illumination. This interface wave with a penetration depth comparable to the light wavelength is created in a total internal reflection geometry. While such experiments were so far restricted to solid-liquid interfaces, we built up a new apparatus for an investigation of the water-air or the water-oil interface. As an essential step, the procedure of optical adjustment and clean sample preparation were optimized to meet the high experimental demands. The scattering contribution of capillary waves depends strongly on the angle of incidence. It can be distinguished from other scattering contributions, e.g. concentration fluctuations close to the interface.

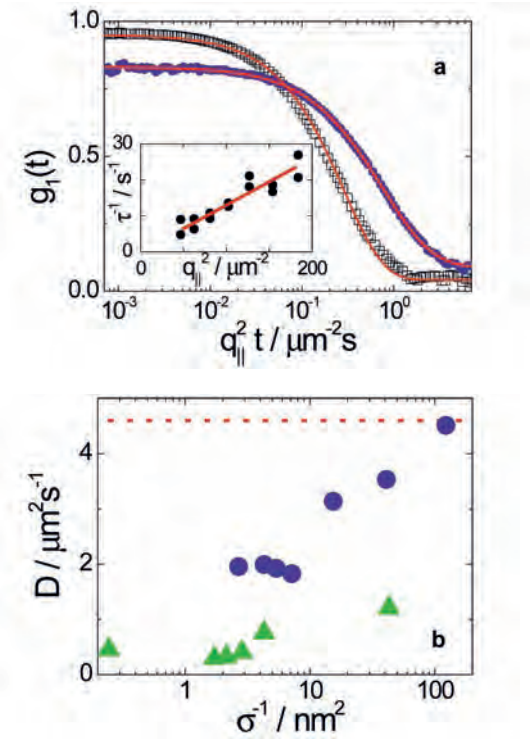


Fig. 3: Dynamic light scattering data of a polyisoprene-polystyrene block copolymer at the water-air and the water-dodecane interface. (a) Comparison of the field correlation function $g_1(t)$ for the water-air interface (•, σ^{-1}=7nm^2) and for bulk scattering (□) versus a reduced time scale. The inset shows the inverse relaxation time τ^{-1} versus the squared scattering vector component tangential to the interface, $q_{||}$. The slope yields the diffusion constant D. (b) D versus the nominal interface area σ^{-1} per molecule for the water-air (•) and the water-dodecane (▲) interfaces. The dotted red line indicates the bulk diffusion of the polymer below the critical micelle concentration.

Target of the investigations was a comparison of the dynamics of a polyisoprene-polyethyleneoxide block copolymer sample at the water-air and the water-dodecane interface. **Fig. 3a** shows field auto-correlation functions for scattering at the water-air interface and in bulk water (concentration below the critical micelle concentration). The quadratic dependency of the inverse relaxation time τ^{-1} on the tangential component $q_{||}$ of the scattering vector, as shown in the inset, hints to a two dimensional diffusion within the interface. The evolution of the diffusion constant D for varying nominal interface area per molecule, σ^{-1}, is depicted in **Fig. 3b**. D decreases with decreasing σ^{-1}. Also included in Fig. 3b is the diffusion of the same polymer at the water-dodecane interface. The lowering of D compared to the air-water interface exceeds the effect expected from the additional friction of the dodecane part. Analogous to data evaluation in bulk light scattering, this can be interpreted as an enhanced two dimensional hydrodynamic radius. For the water-dodecane interface, the diffusing entities consist of several block copolymer molecules.

Colloid Characterization by Bulk Light Scattering

Classical bulk light scattering was applied for the characterization of several colloidal systems. A first example is an investigation of emulsified liquid crystals **[4]**. In addition to a size measurement by dynamic light scattering, temperature dependent depolarized light scattering yields the phase behaviour of the liquid crystal within the droplets. There is a decrease over 20K of the phase transition temperature compared to the bulk value, which, however, probably rather reflects the presence of impurities than effects of finite size or curvature. It was shown, that at finite values of the scattering vector the internal director fluctuations within the droplets affect the dynamic light scattering data.

In cooperation with the biomaterials department, the temperature dependent aggregation of amelogenin nano-spheres was investigated **[5]**. Amelogenin is a biopolymer which plays an essential role in the tooth formation. While small angle X-ray scattering shows that the nano-spheres remain intact as individual entities, dynamic light scattering detects an irreversible aggregation of those nano-spheres above a temperature of 40°C.

R. Sigel, A. Stark, A. Stocco, B. Schonert
sigel@mpikg.mpg.de

References:

[1] Erbe, A., Tauer, K., and Sigel, R.: Ellipsometric Light Scattering for the Characterization of Thin Layers on Dispersed Colloidal Particles. Phys. Rev. E **73**, 031406 (2006).

[2] Erbe, A., Tauer, K., and Sigel, R.: Ion Distribution around Electrostatically Stabilized Polystyrene Latex Particles. Langmuir **23**, 452-459 (2007).

[3] Erbe, A. and Sigel, R.: Tilt Angle of Lipid Acyl Chains in Unilamellar Vesicles. Submitted to Eur. Phys. J. E.

[4] Tongcher, O., Sigel, R., and Landfester, K.: Liquid Crystal Nanoparticles Prepared as Miniemulsions. Langmuir **22**, 4504-4511 (2006).

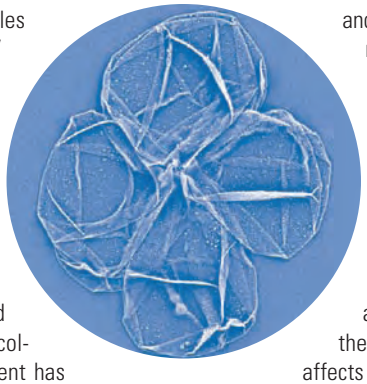
[5] Aichmayer, B., Margolis, H.C., Sigel, R. Yamakoshi, Y., and Fratzl, P.: The Onset of Amelogenin Nanosphere Aggregation Studied by Small-Angle X-Ray Scattering and Dynamic Light Scattering Journal of Structural Biology **151**, 239-249 (2005).


INTERFACES

Research in the Department of Interfaces

I. General Strategy

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



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

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

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

II. Research Highlights

II. 1 Planar Interfaces

Insoluble monolayers at the air/water interface as most suitable model system are made use of in the group of *G. Brezesinski* studying polypeptides, phospholipids, DNA binding and enzymatic hydrolysis and phosphorylation at interfaces, the leading techniques being FTIR-spectroscopy and X-Ray scattering. It is demonstrated for β-amyloid that it changes structure and orientation depending on the lipid density at an interface it is coupled to. For an antibiotic peptide it is shown that it assumes an α-helical conformation upon membrane insertion and at the same time fluidizes the membrane. For studies of peptides successful collaboration with the theory *(V. Knecht)* and the colloid chemistry *(H. Börner)* departments could be developed. The structure, but even more the presence of domain boundaries in lateral phase separation of mixed phospholipid/ cholesterol mixtures has been shown to affect the activity of phospholipases.

The group of *H. Motschmann* could demonstrate by sum frequency spectroscopy that the thiocyanate ion, as a representative chaotropic ion where the interfacial orientation can be determined, affects the water structure at the surface. Its orientation has to be taken into account because most probably a dipolar interaction disorders the water structure.

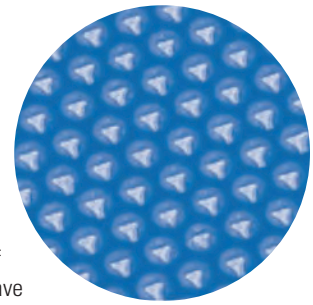
The slow dynamics (< 1 Hz) of mixed protein/surfactant adsorption layers has been the focus of the group of *R. Miller.* They could describe the dilational modulus as a function of frequency for different composition within a model they derived. The group now has also expanded their models to describe the thermodynamics of nanoparticles at fluid interfaces.

Interactions between liquid interfaces and local dynamics are the main topics of the group of *R. Krastev*. For foam films they showed that their drainage can be described by classical theories only down to thicknesses of 40nm. For lower thickness the velocity increases more drastically than expected for constant friction. For polyelectrolyte multilayers containing a phospholipid bilayer they showed that lipid coupling reduces the water content of the multilayer.

Alkanes on solid (SiO_2) surfaces have been the prime interest of the group of *H. Riegler*. These systems are most simple models since they are expected to exhibit only van der Waals interactions. It has been shown that the surface induces crystallization, and the extent is determined by the SiO_2 thickness. Thus studying the melting point increase the interaction potentials could be derived.

II. 2 Non – Planar Interfaces

The hierarchical assemblies of bisterpyridines, metal ions and amphiphiles studied in the group of *D. Kurth* have gained increasing interest and complexity due to the dynamic nature of the modules. Since the molecular weight of the metal containing polyelectrolyte drastically depends on the stoichiometry of the partners this dependence had to be modeled (coop. *T. Gruhn* theory) and studied in detail by analytical centrifugation (coop. *H. Cölfen*, colloid chemistry). As transitions between the phases are accompanied by changes in the coordination geometry they also affect the optical and magnetic properties.



The group of *G. Sukhorukov* has shown the existence of temperature induced shape transitions in polyelectrolyte multilayer capsules. Since the high temperature phase is distinguished by high mobility an equilibrium structure concerning capsule dimensions could be established. It results from a minimization of the surface energy balancing hydrophobic and electrostatic contributions. The latter can be manipulated in a predictable way via pH and salt. It was also shown that capsules can be sensitized toward IR absorption to enable remote release at specific location within a cell.

The glass transition within multilayers has also been verified and quantified by AFM based elasticity measurements in the group of *A. Fery*. At the transition which can be varied via salt and type of polyelectrolyte between 20°C and 90°C the modulus changes by more than two orders of magnitude.

D.G. Shchukin has developed sonochemistry as a new way to prepare multifunctionalized nanocontainers. He also managed to show how to integrate electrochemically responsive containers into coatings.

The group of *D. Wang* functionalizes nanoparticles to direct their organization on different length scales. It is shown that Au nanoparticles can be reversibly switched via pH to move between different solvents and their interface. Arrays of nearly µm sized capsules can on the other hand be used to pattern surfaces or to coat colloidal particles such that they exhibit symmetric interactions into 3D such as sp^2 or sp^3 hybrids.

The control of vectorial electron transfer across thin films and capsule walls has been an issue for a joint effort with TU Berlin *(P. Hildebrandt)* and University Potsdam *(F. Scheller, R. Menzel)* with participation of the groups of *R. Krastev* and *D. Kurth*. There it was shown that electron transfer between chromophores, even if they are 3 nm apart is not mediated by conjugated bonds. The electron transfer between redox active proteins in films is shown to occur directly between these molecules which may provide a means to construct highly specific sensors.

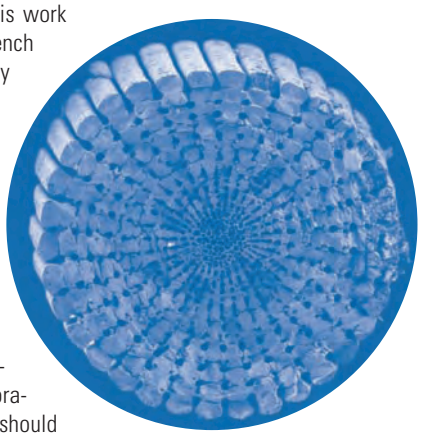
The International Joint Laboratory with the CAS led by *J. Li* has been successful creating capsules existing of polyelectrolytes, phospholipids and the membrane integral channel and motor ATP ase. It could be shown that thus a pH gradient could be converted into ATP.

The collaborative research group together with the Fraunhofer IAP has been active as a partner in surface functionalization of nanoparticles as well as in the synthesis of block copolymers to functionalize planar and curved surfaces. It has been successful in establishing a Campus project on "Bioactive Surfaces" including also the newly settled Fraunhofer Institute of Biomedical Technology.

III. Future Development

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

- *D. Wantke* retired, and a part of his activities have been taken over by the group of *H. Motschmann*
- *A. Fery* has accepted a call to move as professor to the University Bayreuth. His group will cease to exist during this year with 1 or 2 postdocs remaining in the department continuing collaboration with him.
- The group of *G. Sukhorukov* will also expire during this year with the last thesis finishing. Some activities with microcapsules will, however, be continued within the department with postdocs and guests directly associated with the director.
- Towards beginning of next year also *D. Kurth* is expected to leave the department. To continue the activities on supramolecular systems as well as the joint laboratory with NIMS T. Nakanishi has started to work here as group leader.
- *D. Shchukin* won the Nanofuture award which enables him to build-up an own group on self- repairing coatings within the department. Mostly under the guidance of *D. Shchukin* we have also started research towards sonochemistry, the conversion of surface energy into chemistry. This work will be expanded within a joint German/ French laboratory, the French partner being the newly established institute for separation chemistry headed by *T. Zemb* at Marcoule (CEA). In order to intensify this collaboration I have received also the Gay-Lussac award jointly from the French ministry of science and technology and the Humboldt foundation.



Altogether, topics just emerging in the department are sonochemistry and self-repairing coatings, the other themes are in the phase of harvesting. Therefore national and international collaborations have been established. These collaborations should enable a scientific output even increasing although the headcount is expected to decrease from more than 80 to less than 70 persons. Also I expect that this way the funding by EU projects (participation in 6 STREP in the 6th framework programme) may be kept at the same level. Another focus will be to make the campus project "Bioactive Surfaces" a success which means to concentrate studies on molecular interfaces more towards surfaces responsive to switch attachment and function of proteins and cells.

That much of the research is interesting, original and modern the reader may deduce from the next pages. Measuring the success in funding and citations is now fashionable, easy and only partly correct. Although these numbers are very favourable I refrain from listing them because of their limited value. The most important criterion in my view is that many students and postdocs could make a major step in their career which in turn makes further thriving the field of molecular interfaces.

Helmuth Möhwald
Director of the Department of Interfaces

Interactions at Interfaces: Langmuir Monolayers as Model Systems

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)

Monolayers provide a flexible and versatile system to study interactions at surfaces, especially those relevant to biological systems. The behavior of biomolecules, such as lipids, peptides, and DNA, confined in a surface environment can be studied using single- or multi-component monolayers **[1-3]**.

Peptide-Lipid Interactions

Smaller peptides and model systems allow us to study fundamental interactions such as electrostatic effects, hydrophobic interactions, or packing constraints that control peptide behavior at surfaces. The packing and charge density of a monolayer can be easily varied to study the effect of surface composition on peptide behavior.

Small model β-sheet forming peptides are one area of our current focus **[2,4,5]**. This focus stems from their assumed role in diseases (amyloid, peptide of Alzheimer's disease) and novel applications of β-sheet self assembly at the air-water interface. Shorter model peptides allow collaborations with colleagues in the Theory department who perform molecular dynamics simulations and with colleagues in the Colloid department who use peptide self assembly to form novel structures.

Another field of peptide research deals with peptide antibiotics. We use the antimicrobial peptide NK-2, which is a 27 amino-acid residues derivative of the cationic core region of NK-Lysin, a polypeptide of mammalian lymphocytes. A better understanding of the mode of action of these peptides could enhance the design and development of alternatives to the conventional antibiotics.

Results: Infrared Reflectance Absorbance Spectroscopy (IRRAS) and Grazing Incidence X-Ray Diffraction (GIXD) are used to follow the behavior of small β-sheet forming peptides confined in an interfacial environment. Changes in the conformation and orientation of peptides and novel polymer peptide compounds are studied by a combination of traditional IRRAS measurements at the air-water interface, spectral simulations, and 2D IR correlation techniques. **Fig. 1** shows infrared spectra for a peptide, $G(VT)_5$, monolayer in an expanded and highly compressed state. The large increase in only the Amide II band between these two spectra indicates that upon monolayer compression, the β-sheet domains of the

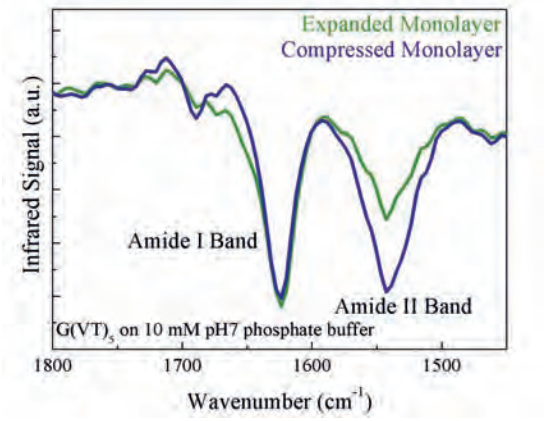


Fig. 1: IRRA spectra of a $G(VT)_5$ peptide spread on 10 mM pH 7 phosphate buffer. The spectra were taken at 20 °C using s-polarized light and an incident angle of 40°. The surface pressures of the expanded and compressed monolayers were 1 and 44 mN/m, respectively.

$G(VT)_5$ peptide change their orientation in the air-water surface plane. Monolayers of pure β-sheet forming peptides are highly crystalline with 2D order. GIXD measurements show the characteristic spacing, 4.76 Å, for β-sheet structures. Additionally, GIXD measurements at higher pH values show that this structure is conserved even when short chains of *pn*BA (poly(n-butyl acrylate) polymer are attached to the peptide, whereas no film structure is seen at low pH. The pH can be used as a switch for this polymer-peptide. The polymer-peptide layers however remain in a fluid like phase unlike the highly crystalline pure peptide film. For the pure peptide film, a Bragg peak that corresponds to a repeat distance equal to the peptide end-to-end distance (45 Å) confirms the crystalline nature of this monolayer.

Adsorption and secondary structure of NK-2 at the air/buffer interface were measured by IRRAS. The peptide reorients from random coil in bulk (CD data) to α-helical structure at the interface. The long axis of the helix is oriented horizontally to the interface. NK-2 adsorption to an anionic monolayer leads to a fluidization of the aliphatic chains (increased transition pressure). The secondary structure of the adsorbed peptide is different (either α-helical with an oblique orientation or random coil) from that observed at the air/buffer interface.

GIXD experiments show that the presence of NK-2 influences the structure of the condensed anionic monolayer. The insertion of NK-2 increases the tilt angle of the lipid molecules.

To assess the location of NK-2 in the lipid matrix, specular X-ray reflectivity (XR) studies were performed. The XR curves are shown in **Fig. 2** with the corresponding electron density profiles. The electron density profile shows that NK-2 adsorbs to the negatively charged monolayer even at high surface pressures.

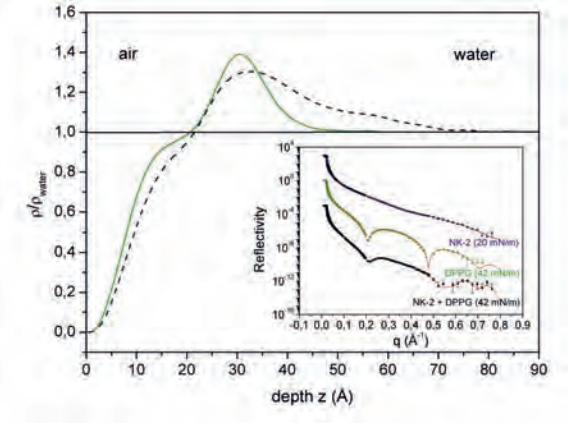


Fig. 2: Electron density profile of 1,2-dipalmitoyl-phosphatidylglycerol (DPPG) on buffer (green line) and on 1 µM NK-2 (black, dashed line) at 42 mN/m and 20 °C. X-ray reflectivity profiles (insert) of 1 µM NK-2 in PBS (10 mM, pH 7.3) adsorbed at the air/buffer interface, DPPG monolayer on PBS and on 1 µM NK-2. Solid lines (red) are the best fits to the experimental data.

Enzymatic Reactions at Interfaces

The application of surface-sensitive techniques permits *in-situ* observations of particular interactions that occur at biological membranes. Thus, the hydrolysis of phosphatidylcholines by different phospholipases can be investigated. We obtained new results on the dependence of the lipid monolayer structure on the action of phospholipase D (PLD) and phospholipase A_2 (PLA_2). Another project, which has been recently started in cooperation with the University of Jena, examines the interaction of the phosphatidylinositol 3-kinase γ (PI3Kγ), which phosphorylates their substrates, with lipid model membranes.

Results: The PLD activity depends on the segregation of the hydrolysis product (phosphatidic acid, PA) within the monolayer. However, no specific structural parameter of the substrate-containing phase, such as the tilt of the lipid chains or the molecular area per head group, is crucial for high hydrolysis rates. Instead, we discovered that the structure of the PA-rich domains is decisive for the activation or inhibition of PLD.

PLA_2 exhibits maximum activity in the simultaneous presence of liquid-expanded and condensed phases. It is therefore concluded that phase boundaries play a crucial role in this process. We revealed that liquid-liquid immiscibility as found in mixed phospholipid/cholesterol monolayers is sufficient to activate the enzyme. This finding involves important progress in the comparison of biophysical observations with physiological conditions as biological membranes naturally occur in a liquid-disordered phase. The eventual formation of liquid-ordered structures implies the occurrence of membrane domains even though the existence of the so-called rafts is still under debate.

The substrates (phosphoinositides) of PI3Kγ have been shown to mediate a large variety of important physiological functions. The properties of phosphoinositides are largely determined by the structure of their head group, which is at physiological pH highly charged but also able to be engaged in intermolecular hydrogen bond formation. One factor that is expected to affect mutual phosphoinositide interactions is the presence of cations with different valence, size, and concentration **[6,7]**.

The DP-PI3P film becomes progressively more expanded with increasing concentrations of monovalent cations (Li^+, Na^+, Cs^+). The tilt angles of the lipids change with the size of the hydrated monovalent cation according to the Hoffmeister series (**Fig. 3**). Smaller hydrated monovalent cations penetrate deeper into the head group region and increase therefore the area occupied by the head groups and the tilt of the molecules. Divalent cations (Mg^{2+} and Ca^{2+}) have a strong condensing effect on the inositide monolayer (**Fig. 3**) and decrease the layer compressibility. The strong influence of Ca^{2+} on DP-PI3P can be explained by a partial dehydration of the PI3P head group and a subsequent complex formation.

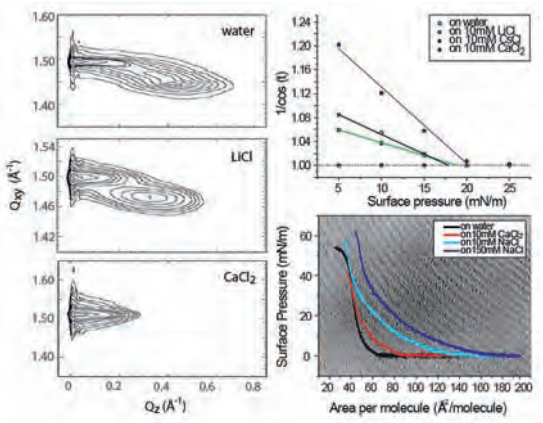


Fig. 3: Left: Contour plots of the corrected X-ray intensities of a DP-PI3P monolayer on different subphases at 10 mN/m. Right: Tilt angle (1/cos(t)) versus lateral pressure (top). BAM picture showing defects within the condensed lipid film with isotherms on different subphases (bottom).

G. Brezesinski, M. Antipina, S. Gromelski, A. Hermelink, A. Muenter, C. Olak, A. Saraiva, K. Wagner
gerald.brezesinski@mpikg.mpg.de

References:

[1] Yue, X., Dobner, B., Limura, K., Kato, T., Möhwald, H. and Brezesinski, G.: Weak first-order tilting transition in monolayers of mono- and bipolar docosanol derivatives. J. Phys. Chem. B **110**, 22237-22244 (2006).

[2] Maltseva, E., Kerth, A., Blume, A., Möhwald H. and Brezesinski, G.: Adsorption of Amyloid b (1-40) peptide at differently charged phospholipid monolayers. ChemBioChem **6**, 1817-1824 (2005).

[3] Gromelski, S. and Brezesinski, G.: DNA condensation and interaction with zwitterionic phospholipids mediated by divalent cations. Langmuir **22**, 6293-6301 (2006).

[4] Rocha, S., Thünemann, A.F., Pereira, M. C., Coelho, M.A.N., Möhwald, H. and Brezesinski, G.: The conformation of B18 peptide in the presence of fluorinated and alkylated nanoparticles. ChemBioChem **6**, 280-283 (2005).

[5] Rocha, S., Krastev, R., Thünemann, A. F., Pereira, M. C., Möhwald, H. and Brezesinski, G.: Adsorption of amyloid b-peptide on modified surfaces: a Neutron reflection study. ChemPhysChem **6**, 2527-2534 (2005).

[6] Maltseva, E., Shapovalov, V. L., Möhwald, H. and Brezesinski, G.: Ionization state and structure of DPPG monolayers at the liquid/air interface. J. Phys. Chem. B **110**, 919-926 (2006).

[7] Shapovalov, V. L. and Brezesinski, G.: Breakdown of the Gouy-Chapman Model for Highly Charged Langmuir Monolayers: Counterion Size Effect. J. Phys. Chem. B **110**, 10032-10040 (2006).

Thin Soft Films

Rumen Krastev 24.01.1960
1985: Diploma, Chemistry (University of Sofia, Bulgaria)
Thesis: Permeability of Gases in Foam Films
1995: PhD, Physical Chemistry of Interfaces (University of Sofia, Bulgaria)
Thesis: Gas Permeability of Black Foam Films
1986: Lecturer in Colloids and Interfaces (University of Sofia, Bulgaria)
1993: Research Specialisation (University of Bristol, UK)
1996-1997: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
2002: Research Scientist (Hahn Meitner Institute, Berlin)
Since 2005: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

When matter is organised in very thin layers (films) the interactions between the film interfaces influence its behaviour. The main aim of our studies is to understand how the strength of the interaction forces modifies the properties of these very thin films. Three types of films are objects of our studies: The foam films – liquid layers which separate two gas phases, wetting films – liquid layers between a gas and solid phase and polymer (polyelectrolyte) films on solid support.

Foam Films

Besides the wonderful play of colours which fascinates children, foam films supply important information about the interaction between fluid (gas/liquid or liquid/liquid) interfaces. We intend to understand how the properties of liquids change when they are confined between two interacting surfaces. Our approach is based on studies of the thinning dynamics of foam films (**Fig. 1**). The foam films consist of an aqueous core sandwiched between two adsorbed surfactant layers. They are generally prepared from a drop of an aqueous surfactant solution. Under the action of capillary pressure (P_C) and attractive interaction forces between the film surfaces, the liquid is expelled from the drop and a film is created. The film thickness, h, decreases until the equilibrium is reached. Usually the thinning process is monitored by measuring the intensity of light reflected from the film with the time, t (**Fig. 1**).

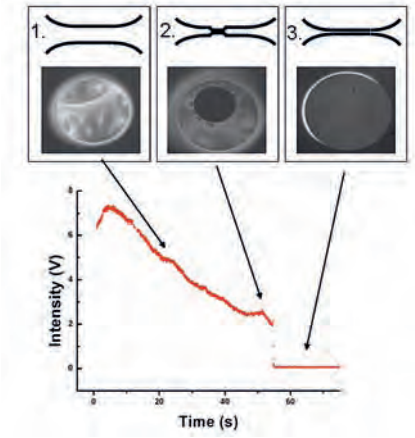


Fig. 1: Intensity of light reflected from the film is directly related to the film thickness. When measured as a function of time it is related to the film thinning dynamics. 1. Thinning foam film; 2. Thinner black spots are formed in the film as a result of the film thinning; 3. The black spots expand, cover the whole film and an equilibrium black foam film is formed.

The thinning of a liquid film between two parallel circular solid disks driven by the pressure P_C is given by the Stefan-Reynolds equation which was later expanded by Scheludko for the case of a disjoining pressure, Π, contribution to the driving force of the thinning:

$$\frac{dh^{-2}}{dt} = \frac{4}{3\eta r^2}(P_C - \Pi(h)) = \alpha_{RE}(P_C - \Pi(h))$$

here η is the viscosity, r is the radius of the film and α_{RE} is the Reynolds coefficient. The model is very simple and does not include disturbances related to the mobility or inhomogeneities of the film surfaces Even though it gives reliable results about the disjoining pressure in the film if the viscosity of the liquid is known.

We performed first experiments on thinning dynamics of foam films stabilised by the non-ionic sugar based surfactant Dodecyl Maltoside ($C_{12}G_2$) at different surfactant concentrations and a constant salt concentration (0.2M NaCl) which assures the formation of very thin black films. We observed that the film thinning follows the Reynolds-Scheludko relation. The coefficient α_{RE} was constant according to the prediction of the equation in a large range of thicknesses down to 40nm. Below this film thickness a strong deviation was observed. The result does not depend on the surfactant concentration. This shows that application of more complicated models for the film thinning which include the surface mobility of the film interfaces will not change the observed effect **[1]**. An example of the dependence of α_{RE} on the film thickness is shown on **Fig. 2**.

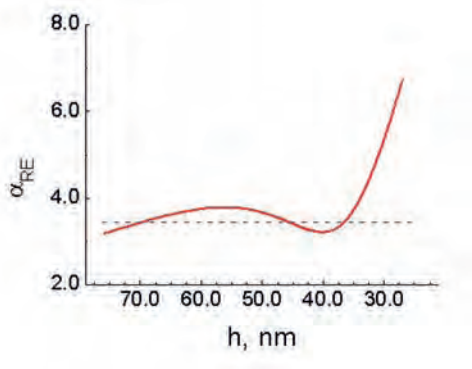


Fig. 2: The Reynolds coefficient α_{RE} as a function of h (red line) for films prepared from 0.06 mM $C_{12}G_2$ and 0.2 M NaCl. Well pronounced deviation from the linear dependence (blue line) is observed in the range of film thickness below 40 nm. The non-linearity above 40 nm is due to the oscillations of the film surfaces deviating from the condition of parallel disks.

One of the main problems when foam films are studied is the position of the plaines of interaction, respectively the thickness of the different layers which form the film. The use of various scattering (reflectivity) techniques allows different tuneable contrast between the layers of the film to be achieved. This way the detailed structure of the film can be found, and the data may be used for precise estimation of the interaction between the film surfaces. We performed first neutron reflectometry experiments with foam films stabilised by tetraethyl ammonium perfluro-octane sulfonate (TAPOS). The contrast between the aqueous film core and the adsorbed surfactant layers was achieved by preparation of the films from D_2O solutions. High quality reflectivity curves were obtained (**Fig. 3**). The detailed structure of the film was found and the position of the counter ions in the film was predicted. Well-defined off-specular signal was registered which is related to correlated oscillations on the film surfaces.

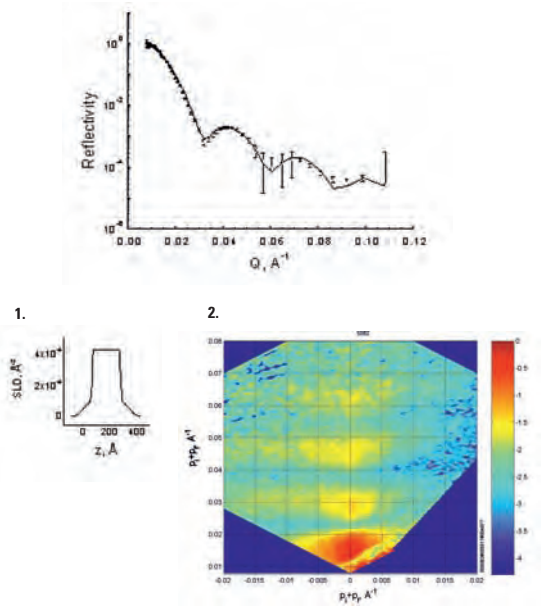


Fig. 3: Neutron reflectometry curve for a foam film prepared from TAPOS. 1. Scattering length density (SLD) profile which gives the best fit to the data; 2. Well-pronounced off-specular signal from the film.

Wetting Films

We studied the stability of aqueous wetting films on hydrophobic support (Teflon) **[2]**. The studies are important when the formation of a three phase contact between solid, liquid and gas phase is concerned. The film stability depends on the acting forces and delivers information about them. We observed a relation between the roughness of the solid phase and the aqueous film stability. Increasing the roughness of the solid support leads to decrease in the film stability. This confirms the strong influence of microscopic gas bubbles entrapped at the solid interface on the film stability. The stability is governed by the interactions of the liquid/air interface with these bubbles. Microscopic foam films are formed instead of direct contact with the solid surface.

Polyelectrolyte Films on Solid Support

The aim of our studies was to understand more about the thermodynamics of thin polymer layers deposited on solid support and to use them as a support to prepare composite materials including layers with different hydrophobic or surface (bio-) active molecules. The thin polymer layers were prepared from polyelectrolytes (PE) organised in multilayers (PEM) using the layer-by-layer dipping deposition technique. We studied the deposition of lipid molecules onto PEM and showed that formation of composit lipid/PEM structures is possible. The process depends on the charge of the PEM and the lipid molecules **[3]**. This proved that the formation of the composites is driven by electrostatic interactions. Proper conditions allowed formation of sandwich like structures composed of a lipid bilayer between two blocks of PEM (**Fig. 4**).

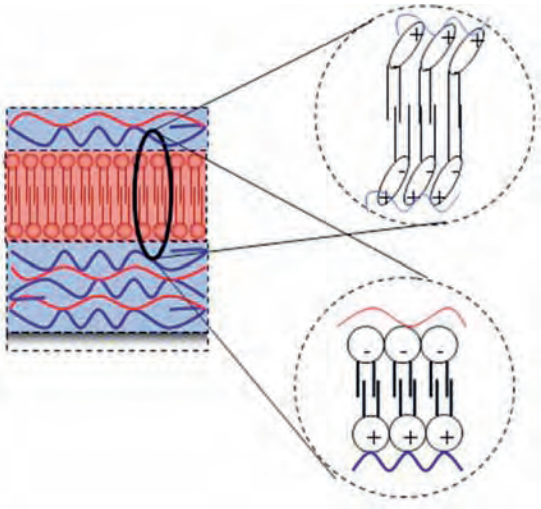


Fig. 4: Lipid layers cushioned onto hydrated PEM. Formation of sandwich like structures or bilayers with asymmetric charge distribution was possible.

Formation of asymmetric lipid layers was also successful which makes possible preparation of composite PEM with separated charges. The difference in the charge density and the hydrophobicity in the structure of such composite PEM will be used in the future to develop new complex materials. Inclusion of a lipid layer leads to decrease in the water content of the PEM. We expect that the effect is related to the modified interactions in the PEM (studies in progress). This effect could be used in future experiments to prepare layers with precisely tuned hydration.

R. Krastev, C. Delajon, J. Chen, H.-J. Müller, M. Kolasinska, N. Mishra, R. Köhler, S. Stöckle,
rumen.krastev@mpikg.mpg.de

References:

[1] Stöckle S., Möhwald H., Krastev R.: Dynamic of thinning of C12G2 stabilised foam films. Coll.&Surf. A (in preparation)

[2] Krasowska M., Krastev R, Rogalski M. and Malysa K.: Air-Facilitated Three-Phase Contact Formation at Hydrophobic Solid Surfaces under Dynamic Conditions. Langmuir **23**, 549-557 (2007).

[3] Delajon C., Gutberlet T., Steitz R., Möhwald H., Krastev R.: Formation of Polyelectrolyte Multilayer Architectures with Embedded DMPC Studied *in situ* by Neutron Reflectometry Langmuir **21**, 8509-8514 (2005).

Dilational Rheology of Mixed Protein-Surfactant Adsorption Layers

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

The addition of surfactants can significantly modify the properties of adsorbed protein layers at liquid/fluid interfaces, leading to changes of the adsorption and rheological characteristics. Although the dilational rheology of proteins or protein/surfactant mixtures is extremely important from a practical point of view, a general theory is still not available. For the much simpler mixtures of two surfactants it appeared to be possible that the rheological behaviour can be described using data for the individual components. The very first attempts to analyze theoretically the rheology of surfactant mixtures were made for example by Lucassen-Reynders, Garrett and Joos. Recently we succeeded in further developing the given theoretical model such that it became applicable to experimental equilibrium and dynamic surface pressure data, for surfactant mixtures as well as for protein-surfactant mixtures **[1]**. For the high frequency limit the thermodynamic quantities are sufficient to describe experimental visco-elasticities **[2,3]**. In this report we describe results of experimental studies of the dilational rheology of a β-lactoglobulin (BLG) mixture with the nonionic surfactant decyl dimethyl phosphine oxide (C_{10}DMPO) at the solution/air interface and its theoretical analysis based on the same model **[4, 5]**.

The main equations for the frequency dependence of the visco-elasticity $E(\omega) = Er(\omega) + i\, Ei(\omega)$ are given by

$$E_r=(PR+QS)/(P^2+Q^2),\ E_i=[PS-QR]/(P^2+Q^2) \qquad (1)$$

and the expressions for the visco-elasticity modulus |E| and phase angle ϕ between stress (dγ) and strain (dA):

$$|E| = \sqrt{(R^2+S^2)/(P^2+Q^2)},\ \phi = a\tan(E_i/E_r) \qquad (2)$$

where P, Q, R and S are parameters containing the oscillation frequency $f=2\omega\pi$, the thermodynamic characteristics and the diffusion coefficients of both compounds **[5]**.

The analysis of the behaviour of mixed systems requires detailed knowledge of the single compounds. In **Fig. 1** the experimental dependencies of visco-elasticity |E| and phase angle ϕ on frequency f is shown for a fixed concentration of the protein. The experimental results are in good agreement with the values calculated from Eqs. (1) and (2) for the surfactant concentration c_S=0 (individual protein solution) and $D_P=10^{-12}$ m²/s. At a frequency of 0.13 Hz the visco-elasticity modulus has almost reached the limiting elasticity value while the phase angle ϕ is close to zero. Note, the given diffusion coefficient D_P is much lower than expected for BLG (about 10^{-10} m²/s). Calculations using such large D_P values do not agree with the experimental data in Fig. 1.

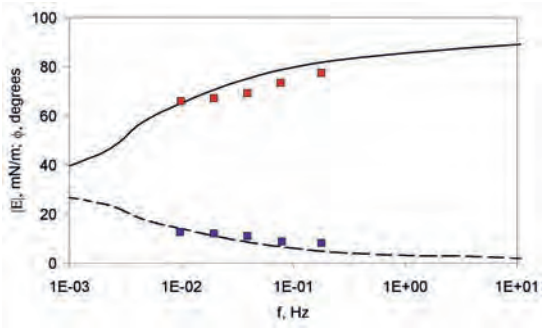


Fig. 1: Dependencies of visco-elasticity modulus |E| (□) and phase angle ϕ (■) on frequency f for a 10^{-6} mol/l BLG concentration calculated from Eqs. (1) at c_S=0; experimental points correspond to data in [5]; the thin curves are calculations for $D_P=10^{-10}$ m²/s.

This shows that in addition to the diffusional exchange with the bulk phase other relaxation effects take place in the adsorption layer, such as molecular reconformation, aggregation, etc. These processes are not analysed yet and the obtained diffusion coefficient has to be seen as an effective value.

Fig. 2 illustrates the dependence of the visco-elasticity modulus on the frequency f calculated for several C_{10}DMPO concentrations. For the theoretical dependencies the realistic surfactant diffusion coefficient of $D_S=3\cdot10^{-10}$ m²/s is used. The frequency increase leads to a monotonic increase of the visco-elasticity modulus |E|. However, its concentration dependence is non-monotonous with a maximum. At the same time, the dependence of ϕ on f decreases monotonously, and at higher C10DMPO concentration larger angles ϕ are observed. The |E| values for C_{10}DMPO calculated from the theory agree satisfactorily with the experimental values (see **[5]**). Note, the good agreement was achieved mainly due to the assumption of an internal compressibility of C10DMPO molecules in the surface layer.

The dependencies of the dilational elasticity modulus |E| on the oscillation frequency at various C_{10}DMPO concentrations in the BLG/C_{10}DMPO mixtures are shown in **Fig. 3** for a fixed BLG concentration of 10^{-6}mol/l. With increasing C_{10}DMPO concentration, the elasticity modulus of the BLG/C_{10}DMPO mixture decreases significantly. For example, at 0.1 Hz the modulus for BLG mixed with 0.7 mmol/l C_{10}DMPO is 20 times lower than that for pure BLG.

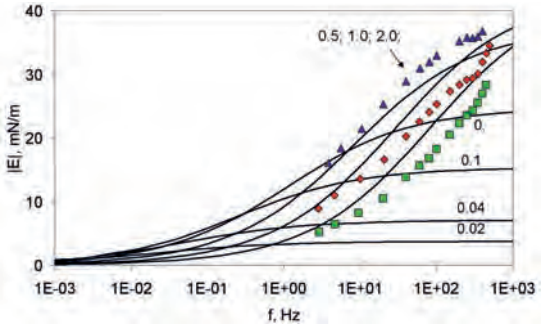


Fig. 2: Surface dilational modulus |E| versus oscillations frequency f for C_{10}DMPO solutions at various concentrations (labels refer to the concentrations given in mmol/l); experimental data for the concentrations: △ 0.5; ◆1; □ 2 mmol/l C_{10}DMPO.

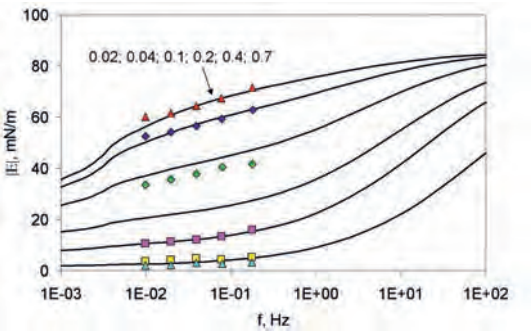


Fig. 3: Dependencies of the dilational elasticity modulus |E| on oscillation frequency f at various C_{10}DMPO concentrations (labels refer to the concentrations given in mmol/l) in the BLG/C_{10}DMPO mixtures; fixed BLG concentration of 10^{-3} mmol/l and ▲0.02; ◇0.04; ◆ 0.1; □ 0.2; ■ 0.4;△ 0.7 mmol/l C_{10}DMPO.

The theoretical dependencies, also shown in **Fig. 3**, were calculated from Eqs. (1) and (2) using the respective parameters of individual BLG and C_{10}DMPO solutions as given in **[5]** and $D_S = 3 \cdot 10^{-10}$ m^2/s and $D_P = 10^{-12}$ m^2/s.

At C_{10}DMPO concentrations above 0.1mmol/l the agreement becomes worse. To obtain better correspondence, one has to use (as one of the possibilities) higher diffusion coefficients for the protein, e.g., $D_P = (10^{-10} - 10^{-11})$ m^2/s instead of 10^{-12} m^2/s. Probably, in presence of a surfactant the processes of protein reconformation and aggregation in the surface layer are accelerated, which increase the corresponding effective diffusion coefficient.

It should be noted that the desorption of BLG from the adsorption layer is extremely slow, and surface oscillations lead to an increase in the adsorbed amount of protein in the surface layer, while desorption of this protein during the surface compression stage can be expected to be very weak. Structural changes, i.e. formation of three-dimensional domains of BLG in the surface layer upon competitive adsorption with a surfactant and displacement of protein due to complex formation were discussed elsewhere.

The dependence of the phase angle φ on frequency f for the BLG/C_{10}DMPO mixture calculated from Eqs. (1) and (2) is shown in Fig. 4. For low surfactant concentrations ϕ monotonously decreases. However, with increasing C_{10}DMPO concentration a maximum in the ϕ vs f curve is observed. Note that the maximum ϕ value increases with the C_{10}DMPO concentration.

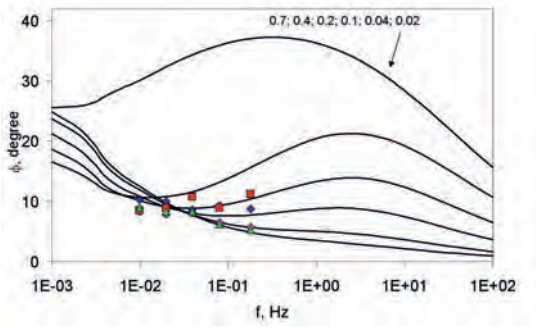


Fig. 4: Dependencies of phase angle ϕ on the oscillation frequency f at various C_{10}DMPO concentrations (labels refer to the concentrations given in mmol/l) in the BLG/C_{10}DMPO mixtures; fixed BLG concentration of 10^{-3} mmol/l and ▲0.02; ◇ 0.04; ◆0.1; □ 0.2 mmol/l C_{10}DMPO.

The last effect is attributable to the increase of the fraction of the area covered by C_{10}DMPO, because for pure C_{10}DMPO solutions in the frequency range studied a viscous behaviour was observed.

It is seen from **Fig. 4** that the experimental phase angle data agree rather well with the theoretical values calculated from Eqs. (1) and (2). For the highest C_{10}DMPO concentrations studied (0.4 and 0.7mmol/l) the scattering of experimental data was very high (in the range of 0° to 50°) because the visco-elasticity modulus was extremely small (2-4 mN/m, see **Fig. 3**). Therefore these data are not shown in **Fig. 4**.

R. Miller, V. Alahverdjieva, J. Ferri, D.O. Grigoriev, J. Krägel, Cs. Kotsmár, S. Siegmund (in close collaboration with E.V. Aksenenko, V.B. Fainerman, V.I. Kovalchuk)
Reinhard.Miller@mpikg.mpg.de

References:

[1] R. Miller, M.E. Leser, M. Michel and V.B. Fainerman: Surface dilational rheology of mixed β-lactoglobulin/surfactant adsorption layers at the air/water interface, J. Phys Chem. **109**, 13327-13331 (2005).

[2] J. Maldonado-Valderrama, M. J. Gálvez-Ruiz, A. Marín-Rodriguez, M.A. Cabrerizo-Vílchez, V.B. Fainerman and R. Miller: Dilatational Rheology of β-Casein Adsorbed Layers at Liquid-Fluid Interfaces, J. Phys. Chem. B **109**, 17608-17616 (2005).

[3] V.I. Kovalchuk, R. Miller, V.B. Fainerman and G. Loglio: Dilational rheology of adsorbed surfactant layers—role of the intrinsic two-dimensional compressibility, Adv. Colloid Interface Sci., **114-115**, 303-313 (2005).

[4] V.B. Fainerman, V.I. Kovalchuk, M.E. Leser and R. Miller: Effect of the intrinsic compressibility on the dilational rheology of adsorption layers of surfactants, proteins and their mixtures, in "Colloid and Interface Science Series", Th. Tadros (Ed.), Vol. 1, Wiley, (2007) 307-333, ISBN 3-527-31462-8

[5] E.V. Aksenenko, V.I. Kovalchuk, V.B. Fainerman and R. Miller: Surface Dilational Rheology of Mixed Adsorption Layers at Liquid Interfaces, Adv. Colloid Interface Sci. **122**, 57-66 (2006).

Ion Distribution at Interfaces

Hubert Motschmann 30.05.1961
1988: Diploma, Chemistry
(University of Erlangen)
Thesis: Numerical and analytical studies on the quantum dynamical equation of Davidov Solitons
1991: PhD, Chemistry
(Max Planck Institute of Polymer Research, Mainz)
Thesis: Scaling and adsorption studies of Block-copolymers
1991-1993: Postdoc
(Eastman Kodak, Rochester, New York)
Since 1994: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

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

The most simple ion specific effect manifests in the surface tension of simple aqueous electrolyte solutions. In general, ions increase the surface tension in a specific manner. The effects are not dramatic; however, due to the simplicity of this system it is crucial for testing the theories. The traditional picture of the interface of an aqueous electrolyte solution is based on a thermodynamic analysis of the equilibrium surface tension iso-therm. The increase in the equilibrium surface tension is then interpreted as an interfacial zone depleted by ions. Recently this picture has been challenged by molecular dynamics simulations using polarizable force fields which predicted that soft ions such as halides are enriched at the interface with a non-monotonic ion profile **[1]**. The key to an understanding of this apparent contradiction lies in a reconsideration of the meaning of thermodynamics. There is no a priori prediction of a profile and thermodynamics can accommodate several conflicting interfacial models provided that the integral excess or depletion is in accordance with Gibbs equation. Therefore, direct experimental observations of molecular structure and energetics of ions in the interfacial region are required.

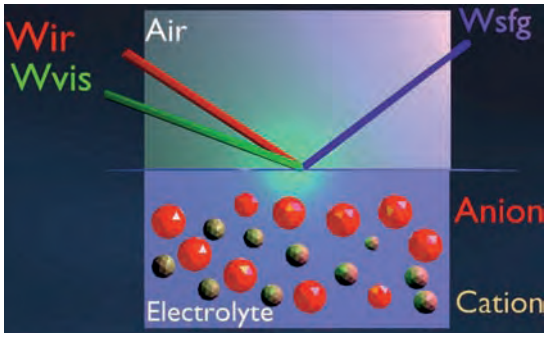


Fig. 1 Scheme of an SFG experiment: The spatial and temporal overlap of an infrared and visible laser pulse generates light at the sum frequency.

We used Infrared-Visible Sum Frequency Spectroscopy (IR-VIS SFG) to study the interfacial composition and structure of aqueous potassium thiocyanate electrolyte solutions **[2]**. The IR-VIS SFG spectra reveal the propensity of the thiocy-anate ions at the air-electrolyte interface.

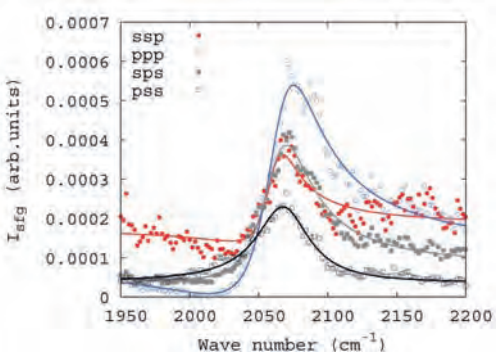


Fig. 2: Vibrational sum frequency spectra showing CN stretch of thiocyanate anion for ~1M potassium thiocyanate solution.The points and continuous lines repre-sent the experimental data and fits respectively.

They also give access to the vibrational features of the interfacial water which are affected by the presence of the ions. Polarization dependent measurements have been used for a determination of the orientation of the pseudo-halide anion. The combined data give a picture of the interfacial architecture on a molecular scale. We believe our current study contributes towards better understanding of this biologically relevant chao-tropic ion and water interactions at the interface. Further our work shows that the orientation of the anion is relevant and needs to be taken into account to get a full picture on the interfacial architecture **[3]**.

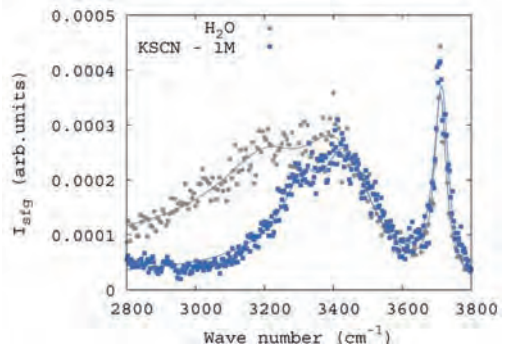


Fig.3: Vibrational sum frequency spectra of water and 1M potassium thiocyanate solution. The points and continuous lines represent the experimental data and fits, respectively.

Surface Rheology

Surface rheology governs a great variety of inter-facial phenomena such as foams or emulsions and plays a dominant role in several technological processes such as high speed coating **[5]**. Its major difference with bulk rheology resides in the high compressibility of the surface phase, which is the direct consequence of the molecular exchange between adsorbed and dissolved species. In analogy to bulk rheology, a complex surface dilational modulus, ε, that captures surface tension changes upon defined area changes of the surface layer, can be defined. The module ε is complex and the molecular interpretation of the dissipative process that gives rise to the imaginary part of the module is subject to some controversy. We used the oscillating bubble technique to study the surface dilational modulus in the mid-frequency range **[6]**. The dynamic state of the surface layer was monitored by a pressure sensor and by surface second harmonic generation (SHG). The pressure sensor measures the real and imaginary part of the modulus while SHG monitors independently the surface composition under dynamic conditions. The experiment allows the assessment of the contribution of the compositional term to the surface dilational modulus ε. Two aqueous surfactant solutions have been characterized; a surface elastic and a surface viscoelastic solution.

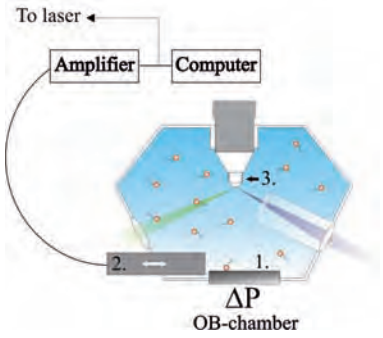


Fig. 4: Cross sectional view of the oscillating bubble device. The piezo translator is immersed in the liquid, the bubble is formed at the tip of the capillary and the pressure is recorded by a sensitive pressure trans-ducer at the bottom of the chamber. The piezo movement leads to an expansion and compression of the surface layer. The surface state can also be probed by Second harmonic generation in total reflection mode.

The elastic surface layer can be described within the framework of the extended Lucassen-van den Tempel model. The change in surface concentration is in phase with the relative area change of the surface layer, which is in strong contrast with the results obtained from the surface viscoelastic solution. Here surface tension, area change and surface composition are phase shifted providing evidence for a nonequilibrium state within the surface phase. The data are used to assess existing surface rheology models **[7]**.

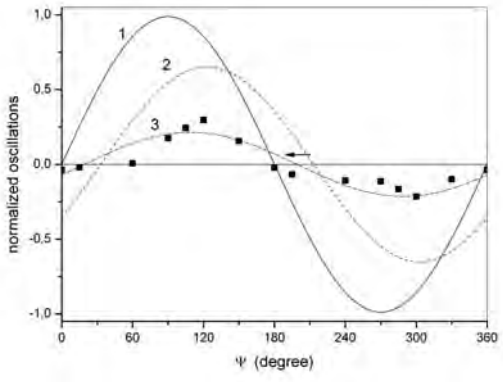


Fig. 5: Dynamic characteristics of surfaces of 4mM DMPB solutions as function of the phase angle. The solid line represents the normalized area change, the dashed line represents the normalized change in dynamic surface tension and the square dots are the changes in the surface coverage measured by SHG

Hubert Motschmann, A. Andersen,
H. Chen, P. Kölsch, P. Viswanath
Hubert.motschmannr@mpikg.mpg.de

References:

[1] Petrov, M., Minofar, B., Vrbka, L., Jungwirth, P. Koelsch, P., Motschmann, H.: Aqueous Ionic and Complementary Zwitterionic Soluble Surfactants: Molecular Dynamics Simulations and Sum Frequency Generation Spectroscopy of the Surfaces Langmuir, **22**(6), 2498, (2006).

[2] Viswanath, P., Motschmann, H: Oriented Thiocyanate Anions at the Air-Electrolyte Interface and its Implications on Interfacial Water – A Vibrational Sum Frequency Spectroscopy Study. J. Phys. Chem. C, Vol. **111**, No. **12**, 4485 (2007).

[3] Koelsch P., Motschmann H.: Varying the counter-ions at a charged interface Langmuir **21**(8), 3436-3442, (2005).

[4] Schneider, M., Andersen, A. , Koelsch, P., Motschmann H.: Following fast adsorption processes with surface plasmon spectroscopy: Reflectivity versus Mismatch Tracking Sensors and Actuators, **104**(2), 276-281, (2005).

[5] Koelsch, P., Motschmann, H.:Relating foam lamella stability and surface dilational rheology Langmuir, **21** (14), 6265-6269, (2005).

[6] Wantke., K.-D., Oertegren, J., Fruhner, H., Andersen, A., Motschmann, H.: The influence of the sublayer on the surface dilatational modulus Colloids and Surfaces A: Physicochem. Eng. Aspects, **261**, 75, (2005).

[7] Andersen, A. , Oertegren, J., Koelsch P, Wantke, D. Motschmann H.: Oscillating bubble SHG on surface elastic and surface viscoelastic systems: New insights in the dynamics of adsorption layers Journal of Physical Chemistry B **110** (37), 18466, (2006).

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

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

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

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?

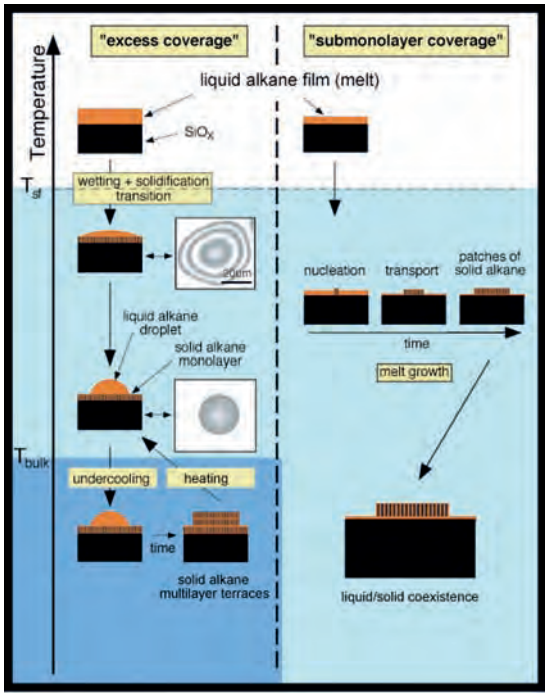


Fig. 1: Various alkane topologies in the case of "excess" coverage (=overall coverage exceeds one mo-lecular length) and "submonolayer" coverage.

Molecularly thin films of long chain *n*-alkanes at solid/gas interfaces show an amazing variety of different topologies (droplets, domains, films, layers, terraces,…) depending on the surface coverage, temperature, and preparation history. For instance, $C_{30}H_{62}$ at SiO_2/air-interfaces shows three temperature regions of distinctly different topologies (**Fig. 1**):

1.) At $T > T_{sf}$ (sf = "surface freezing") all alkane is molten. It forms a completely wetting film of uniform thickness.
2.) In an intermediate range (**Fig. 1**: medium blue back ground), the alkane adjacent to the solid surface solidifies ("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. In the case of "submonolayer coverage", solid domains coexist with liquid (mobile) alkane in between.
3.) Below the bulk melting temperature, Tbulk, in case of excess coverage, the alkane solidifies into multilayers (terraces).

Excess Coverage:
The melting behaviour of the solid multilayers is quite peculiar. At $T_{bulk} < T < T_{sf}$ the melting alkane forms droplets which move **[3]**: They "eat" into the solid terraces while increasing their volume (**Fig. 2**). These "running droplets" are a consequence of mass conservation and autophobicity (the molten alkane forms nonwetting alkane droplets on top of the surface frozen monolayer).

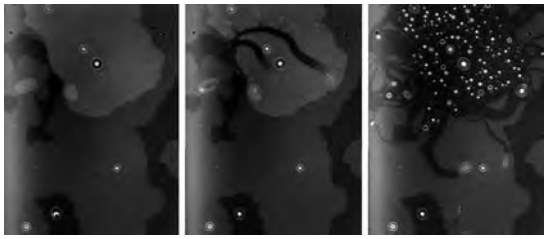


Fig. 2: Droplets of $C_{36}H_{74}$ moving into bilayers (bright grey) and monolayers (medium grey) on top of the surface frozen monolayer (dark grey background). From left to right the temperature was increased continuously (stroboscopic illumination: 10 flashes/frame; area: ≈ 70µm x 50µm).

The droplet speeds are determined by the balance between capillary and friction forces with the melting enthalpy as energy source (**Fig. 3**).

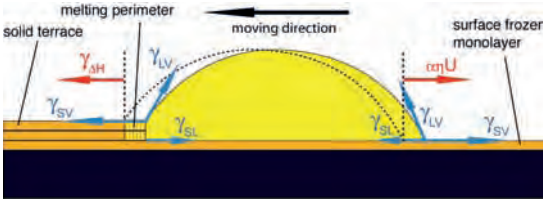


Fig. 3: Forces and energy balance of the moving droplets

Fig. 4 shows the speeds as function of temperature and terrace heights in agreement with the model of **Fig. 3 [3]**.

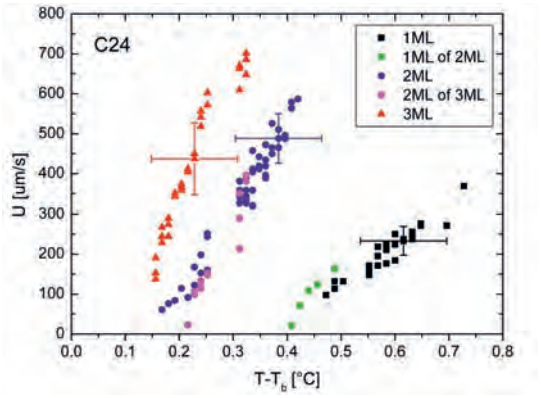


Fig. 4: Velocity vs. temperature for droplets melting into monolayers (1ML), bilayers (2ML), and three melting layers (3ML) of $C_{24}H_{50}$ directly on top of the surface frozen layer. (Tb=bulk melting temperature).

Submonolayer Coverage:

Optical imaging with molecular depth resolution **[4]** allows the online investigation of nucleation and growth of solid, fractal domains (**Figs. 4 and 5**) on the SiO_2/air-interface.

Fig. 5: Submonolayer coverage: Domain growth and alkane flow (arrows) with depletion zone next to the domains.

Depletion zones (**Fig. 6**, darker areas) reveal details on the lateral flow/transport processes in molecularly thin films.

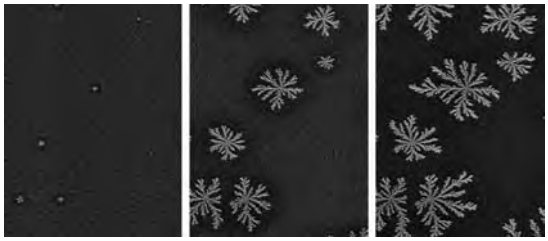


Fig. 6: Submonolayer coverage: Growth of solid al-kane domains upon cooling. Frame size ≈0.6mm x 1mm [4].

A quantitative analysis of the domain size as function of the temperature as well measurements of the alkane coverage in between the solid domains reveals the equilibrium coexistence of solid and liquid alkane over a wide temperature range (**Fig. 7**). This is explained by the contribution of the thickness-dependent interfacial potential to the chemical potential of the alkanes, which leads to a thickness-dependent melting point **[5]**.

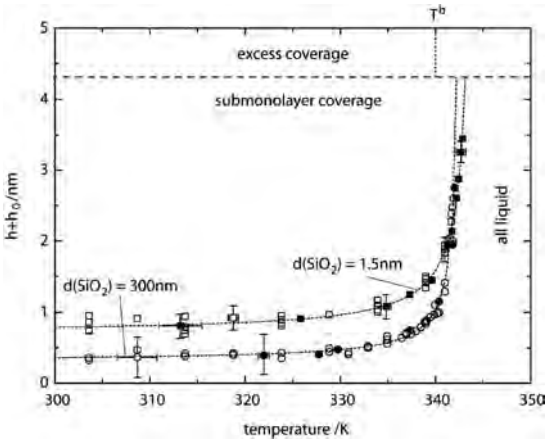


Fig. 7: Phase transition temperatures as function of the thickness of the liquid film in between the domains for substrates with thin (≈ 1.5nm, squares) and thick (≈300nm, circles) SiO_2-layers.

H. Riegler, P. Lazar, R. Köhler
Hans.Riegler@mpikg.mpg.de

References:

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

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

[3] P. Lazar and H. Riegler: Reversible self-Propelled Droplet Movement. A new Driving Mechanism. Phys. Rev. Lett. **95**, 136103 (2005).

[4] R. Köhler, P. Lazar, and H. Riegler: Optical Imaging of Thin Films with Molecular Depth Resolution. Appl. Phys. Lett. **89**, 241906 (2006).

[5] R. Köhler and H. Riegler: Influence of the film thickness on the phase transition temperature of molecularly thin films of long chain alkanes. Phys. Rev. Lett., submitted.

Nanoscale Membranes: Narrowing the Gap between Materials Science and Biology

Andreas Fery 19.03.1972
1996: Diploma Physics
(University of Konstanz)
Thesis: Measurement of sedimentation velocity of colloids
2000: PhD, Physics
(Max Planck Institute for Colloids and Interfaces, Golm)
Thesis: Scanning Force Microscopy on Liquids and its application for characterizing the wetting behaviour of thin liquid crystalline films
2000/2001: Postdoc,
(Institute Curie, Paris)
2001-2006: Group Leader
(Max Planck Institute for Colloids and Interfaces, Golm)
2006: Habilitation,
(University Potsdam)
Thesis: Micro-Mechanics and Adhesion of Artificial Capsules: From Method-development to Understanding Structure-property Relations
Since 2007: Professor
(University of Bayreuth)

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 narrow the gap between these two worlds. In the past two years, we have focused on developing tools for studying mechanical properties in membrane systems, investigating and designing stimuli responsive nanoscale membranes and have taken first steps towards understanding biomimetic motion on colloidal scale and transferring it to artificial systems.

Our main tool for investigating mechanics of membranes is the atomic force microscope (AFM). Using AFM, nanoscale deformations can be applied and a force range between 10s of piko-N up to a micro-N is accessible. During the past years we have applied colloidal probe AFM in combination with optical techniques 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. While originally we were mainly focusing on micron sized microcapsules, we have recently expanded this approach to submicron objects like unilamellar small vesicles **[1]**. As well, we have developed (mostly AFM-based-) techniques for quantifying elastic constants for other membrane geometries like tubes **[2]** (**Fig. 1** displays an example of polymeric tubes made from nanoscale polymeric membranes) or flat membranes. Thus the versatility of the method could be greatly improved.

Going beyond static experiments on mechanical properties, we have explored stimulus sensitivity of polyelectrolyte multilayers in depth. We could for the first time show, that certain polyelectrolyte multilayers exhibit a transition from a glassy material to a viscoelastic fluid upon temperature increase in aqueous environment **[3]**. The glass transition of the multilayer material results in greatly increased deformability as shown in **Fig. 2** and can explain earlier observed shape changes of microcapsules upon heating as surface tension effects. Like on the macroscale, where the success of polymeric materials is largely due to the fact that they can be formed easily at temperatures above their glass transition temperature while being highly form stable below it, this opens new perspectives for shaping nanoscale membranes.

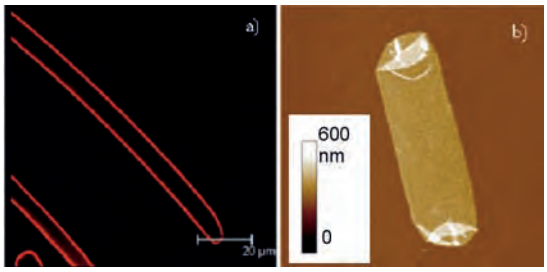


Fig. 1: Microtubes (confocal microscopy image on left hand side with nanoscale membranes as walls (right hand side displays AFM image of a collapsed tube from which the membrane thickness can be derived. Elastic constants can be derived from AFM-based force spectroscopy experiments.

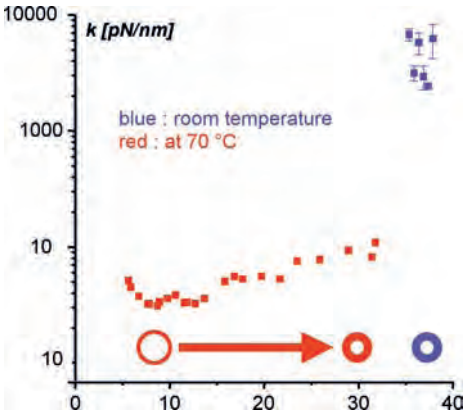


Fig. 2: The stiffness k (slope of the force-deformation characteristic) of an individual microcapsule monitored when first heating and then suddenly cooling the capsule from 70 degrees C to room temperature (semi-logarithmic scale). While at high temperature capsule stiffness gradually increases due to shape changes of the capsule, quenching results in a two orders of magnitude stiffening due to an increase in the material's Young's modulus [3].

While glass transitions are common in polymeric materials, polyelectrolyte multilayers offer alternate possibilities for triggering changes in deformability due to the charge they carry. pH changes can cause charge imbalance and lead to strong capsule swelling due to internal electrical fields. For cross-linked membranes these shape changes are reversible and we could demonstrate that they are accompanied by deformability changes over orders of magnitude **[4]**, offering yet another pathway towards stimuli responsive membrane systems.

One stunning feature of biological microcapsules like bacterial capsids is their ability to move actively and generate forces. We have started studying the mechanisms underlying bacterial movement by investigating in vitro systems **[5]**. In particular, we have focused on the case of motion based on actin gel polymerization/depolymerization like it is employed by listeria monocytes. This mechanism can be well transferred to colloidal particles which are coated by proteins and exposed to suitable solutions. The colloidal particles can – in contrast to their bacterial counterparts – be well controlled in shape and offer thus new possibilities to shed light on the movement process. **Fig. 3** shows a snapshot of colloidal particles actively moving in micro-channels. 3

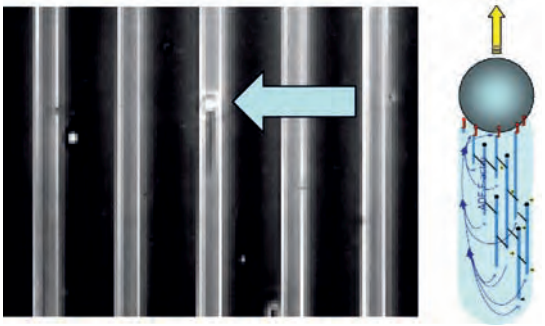


Fig. 3: On the left-hand side, a snapshot of a colloidal particle moving up a microchannel by means of actin polymerization / depolymerization is displayed. Behind the particle (marked with the arrow), a dark cone of actin gel is clearly visible, which is pushing the particle upwards. On the right hand side, a schematic (courtesy M.F. Carlier, Univ. Paris XI) of the underlying actin polymerization / depolymerization process is displayed.

A. Fery, N. Delorme, C. Lu, R. Müller, I. Dönch, M. Nolte, S. Schmidt, L. Kaitan, M. Neeleman
Andreas.fery@mpikg.mpg.de

References:

[1] Delorme, N. and Fery, A.: Direct method to study membrane rigidity of small vesicles based on atomic force microscope force spectroscopy. Phys. Rev. E **74**, 030901 (2006).
[2] Müller, R., Daehne, L. and Fery, A.: Preparation and mechanical characterization of artificial hollow tubes. Polymer, **48**, 2520-2525, (2007).
[3] Müller, R., Köhler, K., Weinkamer, R., Sukhorukov, G. B. and Fery, A.: Melting of PDADMAC/PSS capsules investigated with AFM Force Spectroscopy. Macromolecules **38**, 9766-9771, (2005).
[4] Elsner, N., Kozlovskaya, V., Sukhishvili, S. A. and Fery, A.: pH-Triggered Softening of Crosslinked Hydrogen-bonded Capsules. Soft Matter **2**, 966, (2006).
[5] Schmidt, S., Biesheuvel, P.M., Weinkamer, R., Helfer, E. and Fery, A.: Randon Curvature Motion of Self-Propelled Biomimetic Colloids. Manuscript submitted

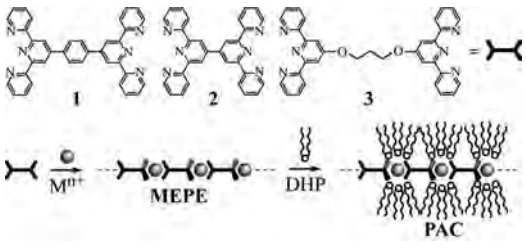
From Molecular Modules to Modular Materials

Dirk G. Kurth 06.11.1964
1990: Diploma, Chemistry (RWTH-Aachen)
Thesis: Preparation, characterization and reactivity of molecular monolayers on metal oxide substrates.
1993: PhD, Chemistry (Purdue University)
Thesis: Synthesis, Reactivity, and Characterization of Thin Organic Films on Metallic Substrates
1994-1996: Postdoc (Université Louis Pasteur, Strasbourg)
Since 1996: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
2003: Habilitation (Potsdam)
Thesis: Self-Assembly of Hierarchically Structured Architectures of Metallo-supramolecular Modules
Since 2004: Director National Laboratory for Materials Science (NIMS), Tsukuba, Japan.

Weak competing interactions provide an efficient and elegant route to self-assemble supramolecular materials with a wide range of value-adding and dynamic properties. Metal ion induced self-assembly is one of the major recognition motives in supramolecular chemistry. The resulting metallo-supramolecular modules possess structural, kinetic, magnetic, optic, electronic, and reactive properties that are relevant for functional devices and materials of technological interest.

Materials built up through weak interactions can assemble, disassemble and reconstruct in a dynamic fashion under ambient conditions. Such materials can be adaptive and responsive. Structure and property are dynamic, that is, they depend on external parameters, such as temperature, pH, solvent, ionic strength or external fields, and in addition such materials have the ability to self-repair, self-anneal and self-correct under ambient conditions.

While polymers based on kinetically inert transition-metal complexes are readily characterized in solution by standard analytical means, polymeric assemblies formed by kinetically labile transition-metal complexes have successfully evaded characterization. Due to the enormous prospects of dynamic polymers, we have taken a detailed look at the formation, self-assembly, structure and properties of dynamic macromolecular assemblies using ditopic bis-terpyridine ligands, e. g. 1,4 bis(2,2´:6´,2´´-terpyridine-4´-yl)benzene and kinetically labile transition metal ions including Fe, Co, Ni, and Zn. A high binding affinity and a well-defined stereochemistry make these building blocks attractive components for the assembly of dynamic and functional metallo-supramolecular coordination polyelectrolytes (MEPEs) (**Scheme 1**) **[1]**. The availability of processable MEPEs has stimulated research concerning composite nanostructures **[2]**, Langmuir and Langmuir-Blodgett **[3]** layers, thin films, capsules, and liquid crystals [4], electrochromic windows **[5]**, and magnetic materials **[6]**.



Scheme 1: Metal-ion induced self-assembly of ditopic bis-terpyridines such as 1, 2, and 3, results in metallo-supramolecular coordination polyelectrolytes (MEPEs). Sequential self-assembly with amphiphiles such as dihexadecyl-phosphate (DHP) results in the corresponding polyelectrolyte-amphiphile complexes (PAC).

In a first approximation, the mean molar mass depends on the concentrations and the stoichiometry of the constituents and is determined by the dynamic equilibrium of association and dissociation. On increasing the concentration, the mean length is shifted to larger assemblies. The theory of self-assembly predicts an exponential growth as a function of concentration. If the stoichiometry of the two constituents, that is the ratio of metal ions to ligands, deviates from one, the length of the aggregates is finite. Above a certain concentration, the length of the aggregates reaches a threshold value and becomes independent of concentration. Based on fundamental principles of thermodynamics we calculated the molar mass (**Fig. 1**). Notably, there is a strong non-linearity for the molar mass at a given concentration in the vicinity of the stoichiometric ratio *y=1*, which is interesting for technological uses including adhesion and power transmission. Qualitatively, these findings were confirmed by viscosity measurements and molar mass determination using analytical ultrazentrifugation. Not surprisingly we also find that MEPE solutions are thixotropic, another property of technological interest.

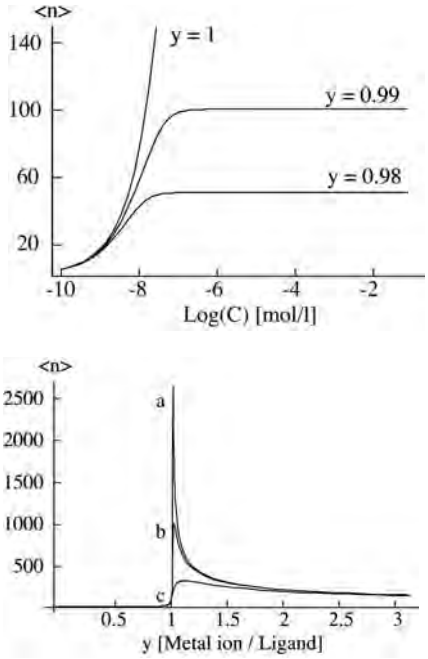


Fig. 1: Average number of monomers per assembly <n> as a function of concentration, C, (top) for different stoichiometries y, and as a function of stoichiometry, y, (bottom) for different monomer concentrations (a: 10^{-3} mol/L, b: 10^{-4} mol/L, c: 10^{-5} mol/L). Here, the stability constants of Fe(II) and terpyridine are used).

The dynamic nature effectively prevents the formation of crystals suitable for structure analysis. Essentially, there is no structural information on the molecular level available for these materials. We were able to grow nanoscopic crystals on surfaces and we were successful in structure determination by electron diffraction. **[7]** The occurrence of metal ions in MEPEs is a fortunate coincidence because they enhance

contrast for diffraction. We have chosen Fe(II) as central metal ion in order to use Mößbauer spectroscopy as complementary tool to probe the coordination environment of the metal complexes. Similar to protein crystallography, we have used a combination of diffraction data and molecular modeling to refine the structure to near atomic resolution. The analysis by electron diffraction reveals a primitive monoclinic unit cell, in which the MEPE forms linear rods, which are organized into sheets (**Fig. 2**). Four sheets intersect the unit cell, while adjacent sheets are rotated by 90° with respect to each other. Mössbauer spectroscopy of bulk samples confirms the pseudo-octahedral coordination geometry and indicates an average length of approximately 8 repeat units in the solid state.

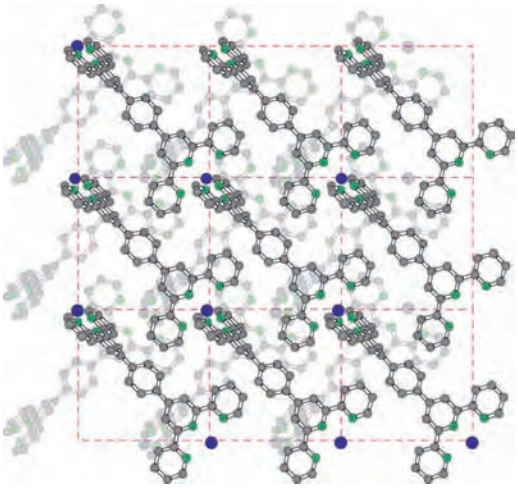


Fig. 2: Structure of MEPE based on $FeOAc_2$ and 1. The MEPE forms linear rods that are organized into sheets. The unit cell consists of four sheets, while each sheet is rotated by 90° with respect to each other. The coordination geometry is pseudo-octahedral.

A route towards mesophases of metallo-supramolecular polyelectrolytes is based on the exchange of the counter ions by suitably charged amphiphilic molecules. Amphiphilic self-assembly of MEPE and negatively charged surfactants such as dehexadecyl phosphate (DHP) affords the corresponding polyelectrolyte-amphiphile complex (PAC) (**Scheme 1**). The combination of rigid-rod polymers and flexible surfactants gives rise to polymorphism. A combination of X-ray scattering and molecular modeling was used to reveal details of the architecture. Notably, DHP forms an interdigitated layer in this structure in contrast to the solid-state structure of DHP and the typical packing motives encountered in amphiphillic architectures. **[8]** The PAC structure is a nice example of a multi-component hierarchical architecture: At the molecular level the structure is determined by the design of the ligands and the metal coordination algorithm. At the mesoscopic length scale structure arises through the interaction of the MEPE rods and the amphiphilic molecules. And finally at the macroscopic level, structure arises through the packing of the PAC rods into the final architecture.

The phase transition in the amphiphilic mesophase is explored to deliberately induce mechanical strain in an assembly of the tightly coupled metal ions in MEPES. Melting of the alkyl chains in the amphiphilic mesophase induces mechanical strain thus in turn distorting the coordination geometry around the central metal ions. As a result, the crystal field splitting of the d-orbital subsets decreases resulting in a spin transition from a low-spin to a high-spin state. The diamagnetic-paramagnetic transition is reversible. Liquid crystalline materials are readily processed into various device architectures, and the concept can be expanded to virtually all metallo-supramolecules polymers with suitable electronic configurations. **[9]**

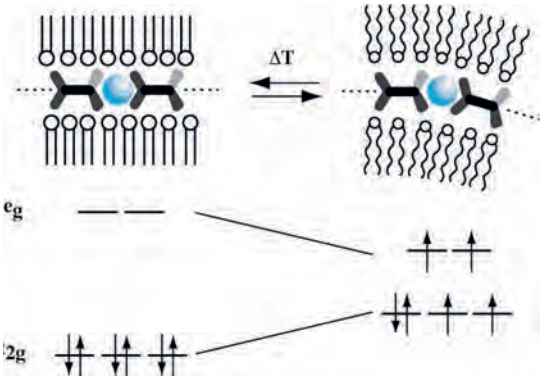


Fig. 3: Melting of DHP in PAC results in a distortion of the coordination geometry (top), giving rise to a reversible spin transition from a low- to a high-spin state (bottom).

Carrying metal ions into macromolecular assemblies may provide a strong impact on polymer chemistry and materials science. It is safe to predict that in the future polymer research will exploit the elements of the entire Periodic Table in systematic ways as weak or strong chain or network forming units. The extension of macromolecular chemistry beyond carbon-based polymers offers unlimited structural possibilities and provides an enormous potential to improve the capacity of macromolecular materials with many new dynamic, thermal, electronic, electrical, photo-electrical, static, mechanical etc. properties **[9]**.

Other areas of interest include structure-property relationships in functional materials based on polyoxometalate clusters **[10]** and fullerenes **[11]**.

D. G. Kurth, V. Friese, R. Dronov, N. Miyashita,
G. Schwarz, T. Sievers, A. Vergin.
kurth@mpikg.mpg.de

References:

[1] D. G. Kurth, and M. Higuchi: Metal ions: Weak Links for Strong Polymers Soft Matter **2**, 915-927 (2006).
[2] D. Akcakayiran, D. G. Kurth, S. Röhrs, G. Rupprechter, and G. H. Findenegg: Self-assembly of a metal supramolecular coordination polyelectrolyte in the pores of SBA-15 and MCM-41 silicate, Langmuir, **21**, 7501-7506 (2005).
[3] P. Lehmann, C. Symietz, G. Brezesinski, H. Kraß, and D. G. Kurth: Langmuir and Langmuir-Blodgett Films of Metallosupramolecular Polyelectrolyte-Amphiphile Complexes, Langmuir, **21**, 5901-5906 (2005).
[4] Y. Bodenthin, U. Pietsch, J. Grenzer, Th. Geue, H. Möhwald, and D. G. Kurth: Structure and temperature behavior of metallo-supramolecular assemblies, J. Phys. Chem. B, **109**, 12795-12799 (2005).
[5] D. G. Kurth, J. Pitarch López, and W.-F. Dong: A new Co(II)-metalloviologen-based electrochromic material integrated in thin multilayers, Chem. Commun., 2119-2121 (2005). (Hot Paper)
[6] D. G. Kurth, U. Pietsch, Y. Bodenthin, and H. Möhwald: Inducing spin crossover in metallo-supramolecular polyelectrolytes through an amphiphilic phase transition, J. Am. Chem. Soc. **127**, 3110-3114 (2005).
[7] U. Kolb, K. Büscher, C. A. Helm, A. Lindner, A. F. Thünemann, M. Menzel, M. Higuchi, and D. G. Kurth: The solid-state organization of metallo-supramolecular polyelectrolytes solved by electron diffraction, Proc. Natl. Acad. Sci. U. S. A. **103**, 10202-10206 (2006).
[8] A. F. Thünemann, D. G. Kurth, M. Beinhoff, R. Bienert, and B. Schulz: V-Shaped Crystalline Structures of Di-n-Alkyl Esters of Phosphoric Acid, Langmuir, **22**, 5856-5861 (2006).
[9] M. Higuchi, A. Hayashi, and D. G. Kurth: Metal Ion Assembly in Macromolecules, J. Nanosci. Nanotech. **6**, 1533-1551 (2006).
[10] S. Liu, D. Volkmer, and D. G. Kurth: Polyoxometalate based Electro- and Photochromic Dual-Mode Devices, Langmuir **22**,1949-1951 (2006).
[11] T. Nakanishi, N. Miyashita, T. Michinobu, Y. Wakayama, T. Tsuruoka, K. Ariga, and D. G. Kurth: Perfectly straight Nanowires of Fullerenes bearing Long Alkyl-Chains on Graphite, J. Am. Chem. Soc., **128**, 6328-6329 (2006).

Biomimetic Vectorial Electron Transfer

Helmuth Möhwald 19.01.1946
1971: Diploma, Physics (University Göttingen)
Thesis: Messungen der absoluten Polarisation optischer Übergänge an Molekülen und Molekülkomplexen in Flüssig-Kristallinen Lösungsmitteln
1974: PhD, Physics (University Göttingen, Max-Planck-Institut für Biophysikalische Chemie, A. Weller, E. Sackmann)
Thesis: Lokalisierte und delokalisierte Triplettzustände in Einkristallen von Elektron-Donor-Akzeptor-Komplexen: ESR- und emissionsspektroskopische Untersuchungen zwischen 4K und 300 K
1974-1975: Postdoc (IBM San Jose)
1975: Research Assistant (University of Ulm)
1978: Habilitation, Physics (University of Ulm)
Thesis: Transporteigenschaften und Phasenübergänge in organischen Charge-Transfer Kristallen
1978-1981: Scientific Coworker (Dornier-System, Friedrichshafen)
1981: Associate Professor C3, Experimental Physics (TU München)
1987: Chair C4, Physical Chemistry, (University of Mainz)
Since 1993: Director and Scientific Member (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 1995: Professor, Physics and Physical Chemistry (University Potsdam)
Since 2001: Honorary Professor (Zheijang University, Hangzhou)
Since 2004: Honorary Professor (Fudan University, Shanghai)
Since 2006: Honorary Professor (Institute of Chemistry at the Chinese Academy of Sciences, Beijing)

Aims

Vectorial electron transfer across a membrane leads in nature to a potential and/ or chemical difference of the two separated compartments, e.g. in photosynthesis or in the respiratory chain. This finally leads to products which store energy or information. Mimicking this process in artificial systems may lead to new types of energy converters or sensors. For most efficient directed electron transfer on one hand the energy levels of donor and acceptor have to be suited (downhill transfer) on the other hand the relative arrangement of the participating groups has to be adapted to maximize a transfer integral. Nature generally uses only one type of chromophore, porphyrin derivatives, (chlorophyll, pheophytin, Fe – containing porphyrins) and optimizes energy levels and orbital overlap by changing the local environment and fixing the groups within a protein matrix. On a much more primitive level we replaced the protein matrix and the lipid membrane by a polyelectrolyte multilayer. Into this we incorporated in project A pyrenes as chromophores with well – known photophysics. Building a film with a polarity gradient by consecutive adsorption of different polyelectrolytes we thus expect that photoinduced electron transfer should occur into only one direction (**Fig. 1**). In project B we incorporate cytochrome c (cyt c) as a well – known electron transfer protein into the film and ask on the influence of the matrix on the electron transfer between protein and electrode as well as between different cyt c.

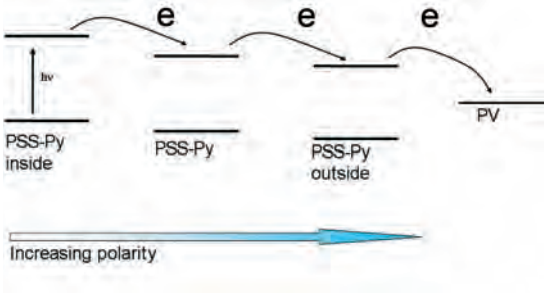


Fig. 1: In this work PSS – Py has been replaced by polyacrylic acid with 3mole% grafted pyrene (PAA – Py)

Results

A – Electron Transfer between Pyrenes

In previous work we have shown that photoinduced electron transfer across the film occurs quantitatively if the average distance between the chromophores is below 3.0 nm, i.e. even in absence of orbital overlap. This surprising result raises the question if the conjugated bond in polystyrenesulfonic acid facilitates the transport by mixing with donor and acceptor orbitals. This so called superexchange mechanism could now be ruled out by building up a film with the only conjugated bonds being those of the chromophore. **Fig. 2** shows that the pyrene fluorescence can be almost completely quenched by adding a polymeric acceptor (PV) that cannot penetrate the film **[1]**.

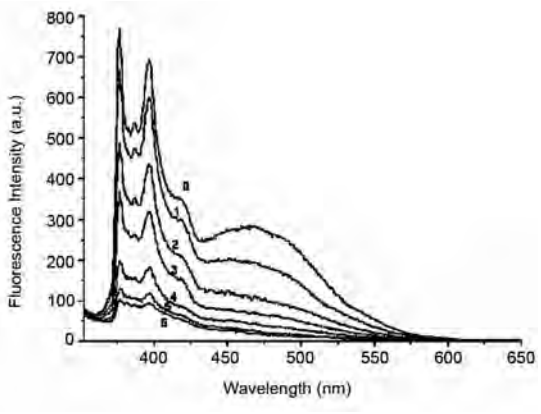


Fig. 2: Fluorescence spectra of multilayers composed of 4 bilayers of PAA – Py and polyallylaminhydrochlo-ride (PAH) at increasing concentrations of polyviolo-gen from 0-6

- The above result can only be understood if the lifetime of the pyrene anion and/ or cation is sufficiently large to enable long – range electron transfer. Indeed in collaboration with the group of R. Menzel (University Potsdam) we could show by time resolved absorption spectroscopy that the lifetime of these ions exceeds 10 µsec, and is even further increased in case of a polarity gradient. **[2]**
- In photopotential measurements with multilayers it was also shown that the lifetime of charge carriers and hence the potential can be drastically increased by going from a symmetric to an asymmetric film (**Fig. 3, [3]**). For the symmetric film switching on and off illumination the photovoltage changes by 4 mV within less than 2 min, whereas for the film with polarity gradient the change is more than an order of magnitude larger, and on switching off the light the photovoltage decay takes more than 30 minutes. This indicates that also charges that have relaxed into deep traps are released at times depending on the local environment.

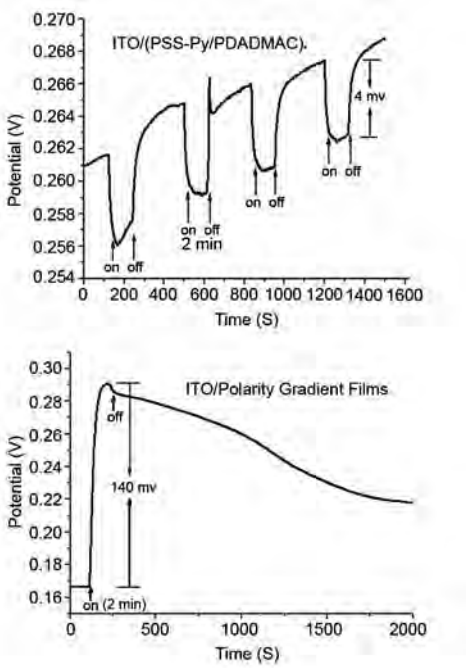


Fig. 3: Photopotential of a polyelectrolyte film containing PSS – Py before and after illumination at 355 nm measured between 0.1 M KCl solutions and an ITO electrode. Fig. 3a: 4 bilayers of PSS – Py and Polydiallyldimethylammonium chloride (PDADMAC). Fig. 3b: polarity gradient film existing of 4 bilayers of PSS – Py/ PDADMAC followed by 4 bilayers of PSS – Py/ PAH and then PSS – Py/ polyethylenimine.

B – Electron Transfer Involving Cyt c

• In collaboration with the group of P. Hildebrand (TU Berlin) the electron transfer between cyt c and rough Ag electrodes was studied by surface enhanced resonance Raman spectroscopy. It was shown that depositing the cyt c on a defined polyelectrolyte film causes a mixing, and hence the desired layered geometry is lost **[4]**. It is also shown that the polyelectrolyte environment influences the detailed mechanism of the electron transfer process. The intermixing may be caused by the rough support necessary to apply this technique.

• In collaboration with the group of F. Scheller (University Potsdam) we have previously shown by cyclovoltammetry that not only cyt c near the electrode but also that within a 10nm thick film contributes to the electron transfer **[5]**. The initial aim was to achieve this by connecting the cyt c via conducting polymers inserted into the film. However, it turned out that this is not necessary, because the cyt c appears to assume proper relative orientation to enable efficient electron transport. This principle has recently been extended to prepare an efficient electron transfer chain with cyt c being a mediator between a redox enzyme and an electrode. (**Fig. 4, [6]**) This may become a new concept for biosensors because coupling different enzymes, again in analogy to nature, enhances the specificity, and having more partners in the film than in a monolayer enhances the sensitivity.

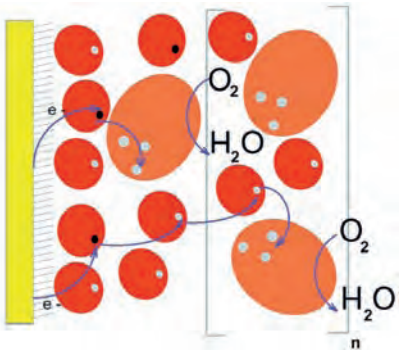


Fig. 4: Representation of the redox reaction chain at cytochrome c/bilirubin oxidase (cyt.c/BOD) electodes. Red circles = cyt.c molecules, ellipses = BOD molecules, arrows indicate electron transfer pathways between cyt.c and BOD within the polyelectrolyte network to enable four-electron oxygen reduction process.

Future Work

Project A has been terminated, but similar experiments are planned with porphyrines and their aggregates in polyelectrolyte films. This would bring the system closer to biology and also enable Resonance Raman spectroscopy. In addition other gradients will be prepared by incorporating also asymmetric lipid bilayers in cooperation with the group of R. Krastev.

In project B the quantitative coupling of different enzymes and thus of reactions appear most promising. Raman spectroscopy has been shown to be a most suitable tool to study the electron transfer mechanisms. However, the need of rough Ag electrodes is very problematic because of their influence on film structure. Therefore in order to avoid the artefacts we intend to deposit Ag or Au nanoparticles on the film to achieve the plasmon enhancement and thus to be able to use smooth supports.

H. Möhwald, WF. Dong, R. Dronov, L. Li
moehwald@mpikg.mpg.de

References:

[1] Li, L., Q. Cui, H. Möhwald: Multilayers Composed of Poly (acrylic acid) Labeled with Pyrene Functionalized for Electron Transfer, unpublished.

[2] Li, L., H. Möhwald, C. Spitz, D. v. Seggern, M. Mucke, R. Menzel: Long-Lived Photoinduced Charge Separation Inside Polarity Gradient Capsules, Adv. Mater., **17**, 2247-2249 (2005).

[3] Li, L., Q. Cui, F. Wu, H. Möhwald: Photoinduced Voltage Changes Inside Polarity Gradient Films, Coll. Surf. A, in press.

[4] Weidinger, IM, DH. Murgida, WF. Dong, H. Möhwald, P. Hildebrandt: Redox Processes of Cytochrome c Immobilized on Solid Supported Polyelectrolyte Multilayers, J. of Phys. Chem, B **110**, 522-529 (2006).

[5] Beissenhirtz, M.K., F. W. Scheller, W. F. M. Stöcklein, D. G. Kurth, H. Möhwald, F. Lisdat: Electroactive cytochrome-c-multilayer in a polyelectrolyte assembly, Angew. Chem., **116**, 4457-4460 (2004).

[6] Dronov, R., D.G. Kurth, H. Möhwald, F.W. Scheller, F. Lisdat: Communication in a Protein Stack: Electron Transfer beween Cytochrome c and Bilirubin Oxidase within a Polyelectrolyte Multilayer, Subm.

Active Coatings Based on Incorporated Nanocontainers (Nanofuture Group)

Dmitry Shchukin 11.11.1976
1998: Diploma, Physical Chemistry (Belarusian State University, Minsk, Belarus)
Thesis: Electrochemistry of conductive polyaniline films
2000: Research Stay, Ecole Centrale de Lyon, France
2001/2002: DAAD fellow (Max Planck Institute of Colloids and Interfaces, Potsdam)
2002: PhD, Physical Chemistry (Belarusian State University, Minsk, Belarus)
Thesis: TiO_2-based composite photocatalysts
2003: Postdoc, Louisiana Tech University, Ruston, USA
2004: Alexander von Humboldt Fellow (Max Planck Institute of Colloids and Interfaces, Potsdam)
2005/2006: Incoming Marie-Curie Fellow (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2006: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Development of a new generation of multifunctional coatings, which will possess not only passive functionality but also active and rapid feedback activity in response to changes in local environment, is a key technology for fabrication of future high-tech products and functional surfaces **[1,2]**. These new multifunctional coatings should combine passive components inherited from "classical" coatings (barrier layers) and active components, which provide fast response of the coating properties to changes occurring either in the passive matrix of multifunctional coatings (e.g., cracks, local pH change) or in the local environment surrounding the coating (temperature, humidity) (**Fig. 1**). The coatings should also have several functionalities (e.g., antifriction, antifungal, and anticorrosion) exhibiting synergistic effects.

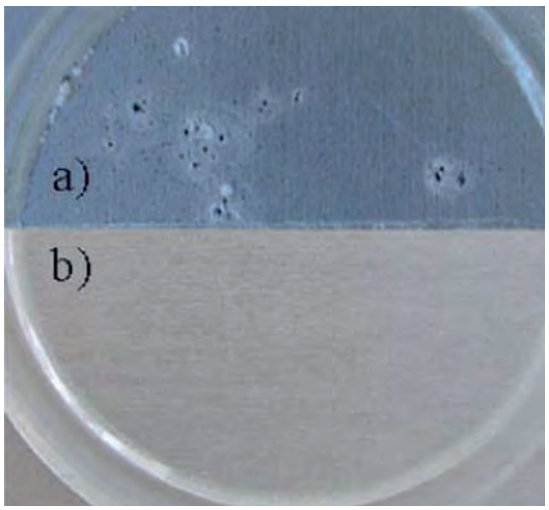


Fig. 1:. Aluminium substrate coated with ZrO_x/SiO_x sol-gel film after 14 days in 0.005 M NaCl (a) and ZrO_x/SiO_x sol-gel film impregnated with benzotriazole-loaded SiO_2 nanocontainers after 14 days in 0.5 M NaCl (b)

The most important part in the design of new active coatings is to develop nanocontainers with good compatibility to the matrix components, possibility to encapsulate and upkeep active material and permeability properties of the shell controlled by external stimuli. The nanocontainers should also be of a size less than 300-400 nm. The nanocontainers of larger size can damage the integrity of the coating matrix forming large hollow cavities, which reduce the passive protective properties of the coating. Depending on the nature of the sensitive components (e.g., weak polyelectrolytes, metal nanoparticles) introduced into the container shell, reversible and irreversible changes of the shell permeability can be induced by various stimuli: variation of the pH, ionic strength, temperature, ultrasonic treatment, alternating magnetic field, electromagnetic fields. Different responses of the container shell can be then observed varying from fine effects like tuneable permeability to more drastic ones like total rupture of the container shell.

Perspective nanocontainers can be divided into two families regarding their mechanical properties and compatibility with the passive matrix of the coating: (i) organic nanocontainers for organic films and (ii) inorganic or composite nanocontainers for mostly oxide-based sol-gel or metal coatings. Most promising nanocontainers (considering their shell stability and versatility of the shell modification) can be fabricated by three general approaches. The first one is based on self-assembly of amphiphilic block copolymers into spherically closed nanostructures followed by cross-linking to stabilize the nanocontainer shell. The second procedure comprises layer-by-layer assembly of oppositely charged species on the outermost surface of dense template nanoparticles using polyelectrolytes, conductive polymers, biopolymers, carbon nanotubes, viruses, lipid vesicles, and nanoparticles as constituents of the nanocontainer shell. The third approach involves the use of ultrasonic waves to fabricate inorganic and composite hollow nanospheres. In this case, a cavitation microbubble is employed as a template on whose surface an inorganic shell is formed from precursors or pre-formed nanoparticles adsorbed at the gas/liquid interface.

Self-organizing block copolymer nanocontainers provide the possibility of entrapping hydrophobic inhibitors, oils or bioactive materials in the core making them dispersed in water. The sizes of nanocontainers can be varied from nanometres to hundreds of nanometres by changing the molecular weight of the polymer and the ratio between the block sizes. The polymer shell can be stabilized by cross-linking or electrostatic deposition of polyelectrolytes and nanoparticles.

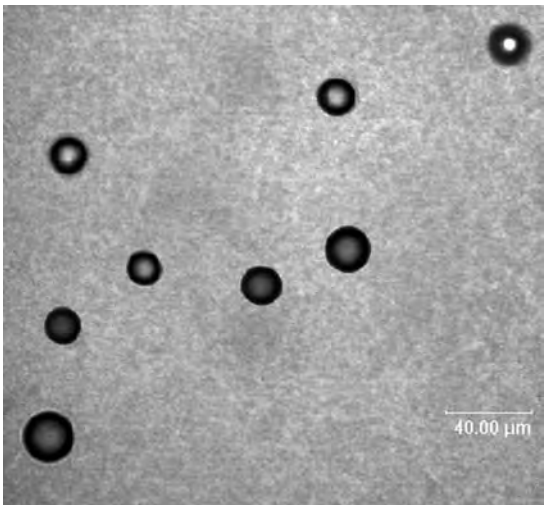


Fig. 2: Confocal microscopy images of the air-filled nanostructured silica spheres made in bright field mode. Silica shell has quartz crystal phase.

Another type of functional nanocontainers can be fabricated by Layer-by-Layer assembly of oppositely charged species **[3]**. The universal character of the method does not have any restriction on the type of the charged species employed for shell construction. The precision of one adsorbed layer thickness is about 1 nm. The shell of the polyelectrolyte nanocontainers is sensitive to a variety of physical and chemical conditions of the surrounding media (pH, ionic strength, irradiation, magnetic field, etc.).

Fabrication of inorganic nanocontainers was demonstrated using the interface of the cavitation bubble as a template **[4]**. Hollow inorganic spheres can be formed by either ultrasonically induced reactions between initial precursors (e.g., salts) at the gas/liquid interface of the cavitation bubble or by melting (or sonoinduced welding) and condensation of the as-prepared and surface-modified nanoparticles at this interface (**Fig. 2**). Acoustic cavitation appears in the liquids at high and moderate intensities of ultrasonic irradiation. The minimum power intensity required for ultrasonic cavitation increases with increase of the frequency of ultrasound. The liquid expands during the expansion by the sound field ("negative pressure"). This results in rapid growth of the weak sites of the liquid predominantly containing dissolved gases ("cavitation nuclei") thus producing vapor and gas-filled cavities or microbubbles. Then, the liquid compresses during the compression phase of the sound field ("positive pressure"). The bubbles continue to grow during the negative/positive cycles until reaching a critical diameter, which depends on ultrasound frequency and nature of the liquid.

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

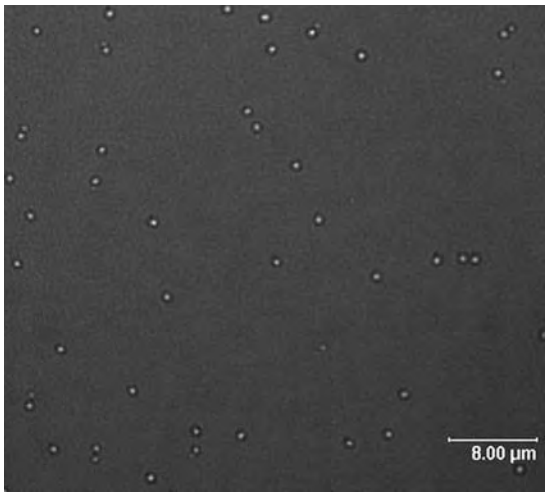


Fig. 3: Confocal microscopy images of toluene-loaded polyglutamate/polyethylene imine/polyacrylate containers in aqueous phase in bright field mode. Average diameter of the containers is 600 nm.

An approach for facile entrapment of the hydrophobic active materials inside polyelectrolyte nanocontainers dispersed in water phase was developed combining ultrasonic technique and Layer-by-Layer assembly protocol. Polyglutamate/polyethyleneimine/polyacrylate nanocontainers loaded with the hydrophobic dye 5,10,15,20-tetraphenylporphin dissolved in toluene were fabricated (**Fig. 3**). About 600 nm in diameter, uniform, stable and monodisperse nanocontainers were obtained. The hydrophobic core of the nanocontainer might contain a big variety of water-insoluble active materials (e.g., drugs, corrosion inhibitors, lubricants) and the outer polyelectrolyte shell has controlled permeability and desired multifunctionality and enables dispersion of the inner hydrophobic content in hydrophilic environment. Addition of the surface-active material (sodium dodecyl sulfate) on the ultrasonic preparation stage leads to a 10-fold increase of the amount of nanocontainers, their monodispersity and stability. Surface active material sharply decreases the surface tension at the interface of the cavitation microbubble prolonging its lifetime thus allowing more dissolved polyglutamate molecules to be condensed at the cavitation interface.

D. Shchukin, M. Prevot, K. Köhler,
D. Radzuik, X. Teng, A. Praast
dmitry.shchukin@mpikg.mpg.de

References:

[1] D.G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M.G.S. Ferreira, H. Möhwald. LbL nanocontainers for self-healing corrosion protection. Adv. Mater. **18**, 1672-1678 (2006).

[2] D.G. Shchukin, M. Zheludkevich, H. Möhwald. Feedback active coating based on incorporated nanocontainers. J. Mat. Chem. **16**, 4561-4566 (2006).

[3] D.G. Shchukin, K, Köhler, H. Möhwald. Microcontainers with electrochemically reversible permeability. J. Am. Chem. Soc. **128**, 4560-4561 (2006).

[4] D.G. Shchukin, H. Möhwald. Sonochemical nanosynthesis at the engineered interface of a cavitation microbubble. PCCP, **8**, 3496-3506 (2006).

Multifunctional Polymer Micro-Capsules

Gleb Sukhorukov 01.05.1969
1991: Diploma, Department of Physics (Lomonosov Moscow State University), Speciality; Biophysics
1994: PhD in Physico-Mathematical sciences (Lomonosov Moscow State University) Thesis: Formation and Investigation of multilayer films containing nucleic acids
1994-1999: Research Scientist at Institute of Crystallography, Russian Academy of Science, Moscow
1995-1996: Research Stay at the Institute of Physical Chemistry, University of Mainz
1998-2000: Postdoctoral Researcher at Max Planck Institute of Colloids and Interfaces, Potsdam
2001: Project Manager at Capsulution Nanoscience AG, Berlin
2002-2005: Group Leader at the Max Planck Institute of Colloids and Interfaces, Potsdam
2005: Professor. Department of Materials, Queen Mary University of London, UK

Polyelectrolyte multilayer capsules continuously attract interest due to a number of fundamental and applied aspects of research. In last years we studied temperature and pH behavior of capsules, guiding permeability and optical addressing to capsule properties as well as were aiming to deliver the capsules to cells and monitoring capsule in living cells.

The temperature-dependent behavior of polyelectrolyte multilayer microcapsules in aqueous environment was investigated from the fundamental point of view, but also with respect to possible applications. To obtain reliable results of pure multilayers, silica particles were introduced as routine templates for capsule preparation and the coating as well as the core dissolution process was optimized for each system used. As studied by a variety of physical methods the influence of different parameters, e.g. type of the used polyelectrolytes, layer number, sequence of layering, charge balance, molecular weight of the polyions, capsule size, cross-linking, and degree of aggregation on the thermal response of capsules were found to have tremendous influence on temperature behavior of capsules (**Fig. 1**) **[1]**.

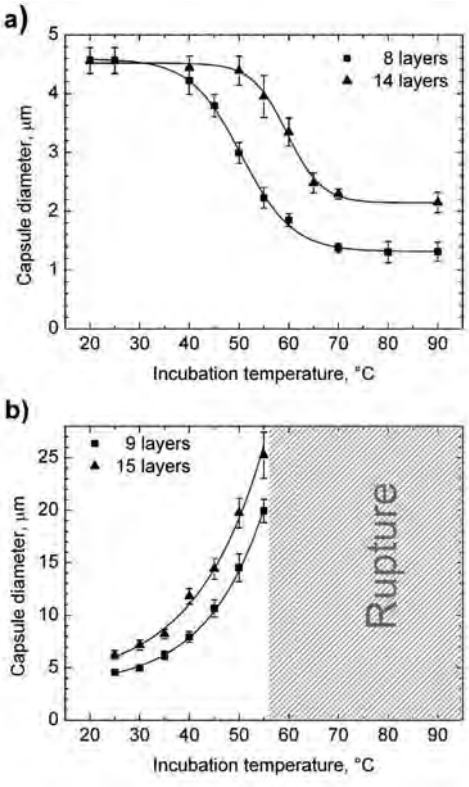


Fig. 1: Quantification of the shrinkage and swelling of PDADMAC/PSS capsules with even (a) and odd (b) layer numbers.

Differential scanning calorimetry measurements of capsules revealed that multilayers undergo a glass transition in water, at which the polymer material softens allowing rearrangements to occur. The state of lowest free energy of the capsules is decisively determined by the interplay between hydrophobic and electrostatic forces and thus the total charge of the shell. Depending on this charge either surface tension, due to an unfavorable polymer/solvent interaction, or electrostatics dominate, leading to a shrinkage or expansion and subsequent rupture of capsules, respectively, at temperatures above the glass transition temperature (T_g). For swelling capsules the force balance can be shifted by the addition of salt and subsequent screening of charges, which enables a reversible switching between shrunk and swollen states. The shrinkage of capsules is accompanied by a wall thickness increase. At the end-point capsules form dense smooth spheres. A new method to quantitatively analyze transmission X-ray micrographs of capsules recorded in aqueous environment indicates that the multilayer walls loose about 40% of their water content during capsule shrinkage.

As the permeability of the shells is distinctly decreased after heating due to the wall thickness increase and densification, a simple and universal encapsulation technique based on the heat treatment of capsules was developed. This new method allows the entrapment of differently charged molecules within a broad range of molecular weights into various kinds of capsules. The encapsulated amount has been quantified. It could be shown that polyelectrolyte multilayer capsules can fuse at temperatures far above T_g or at ionic strength far above the glass transition ionic strength without leakage of their content. From the microscopic snapshots a proper model based on different forces acting on the shells and temperature and salt induced fusion are proposed.

Due to potential applications in the fields of sensors or actuators, stimulable microcontainers and controlled drug delivery. Polyelectrolyte microcapsules containing stimuli-responsive polymers have been prepared with the focus on pH-sensitivity and carbohydratesensing.

First, pH-responsive polyelectrolyte capsules were composed of poly(allylamine hydrochloride) (PAH) and poly(methacrylic acid) (PMA) or poly(4-vinylpyridine) (P4VP) and PMA and varied considerably in their hydrophobicity and the influence of secondary interactions. These polymers were assembled onto $CaCO_3$ and SiO_2 particles with diameters of 5 *µm*. Capsules were stable over a wide pH-range and exhibited a pronounced swelling at the edges of stability, which was attributed to uncompensated positive or negative charges within the multilayers. The swollen state could be stabilized when the electrostatic repulsion was counteracted by hydrogen-bonding, hydrophobic interactions or polymeric entanglement. This stabilization made it possible to reversibly swell and shrink the capsules by tuning the pH of the solu-tion (**Fig. 2**) **[2]**. The pH-dependent ionization de-gree of PMA was used to modulate the binding of calcium ions. In addition to the pH-sensitivity, the stability and the swelling degree of these capsules at a given pH could be modified, when the ionic strength of the medium was altered. A theoretical model was proposed to explain the pH-dependent size variations that took into account an osmotic expanding force and an elastic restoring force to evaluate the pH-dependent size changes of weak polyelectrolyte capsules.

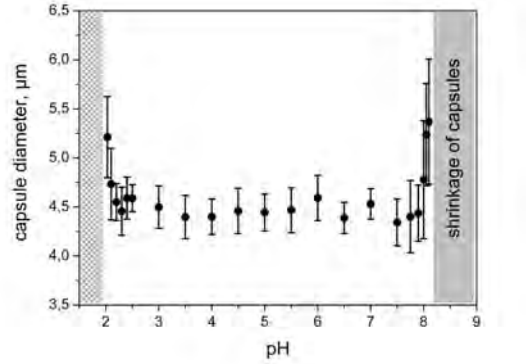


Fig. 2: Diameter of (P4VP/PMA)5 capsules as a function of pH (a). The shaded area indicates the region in which the capsules dissolved (pH < 2). At pH > 8.1 the capsules shrunk to particle-like structures.

Second, sugar-sensitive multilayers were assembled using the reversible covalent ester formation between the polysaccharide mannan and phenylboronic acid moieties that were grafted onto poly(acrylic acid). The resulting multilayer films were sensitive to several carbohydrates, showing the highest sensitivity to fructose. The response to carbohydrates resulted from the competitive binding of small molecular weight sugars and mannan to the boronic acid groups within the film, and was observed as a fast dissolution of the multilayers,when they were brought into contact with the sugar-containing solution above a critical concentration. It was also possible to prepare carbohydrate-sensitive multilayer capsules, and their sugar-dependent stability was investigated by following the release of encapsulated rhodamine-labeled bovine serum albumin.

To drastically decrease the permeability of polyelectrolyte multilayered capsules and, therefore to make them enough efficient for encapsulation of small molecular species a perspective approach is based on use of dense polymers (polypyrrole) **[3]**. The polyelectrolyte shell modified by polypyrrole provides the capsule shell with water-resistant and sufficient barrier properties. However, relevant high brittleness of polypyrrole coatings demands more gentle capsule processing conditions. Magnetite iron oxide nanoparticles were used as a shell constituent to provide the capsules with magnetic properties and, therefore, to propose a mild technical protocol for capsule treatment.

Polyelectrolyte capsules containing metal (Ag- or Au-) nanoparticles in the shell are addressable optically. Focusing a laser on the capsule leads to capsule wall rupture. The potential of this method has been demonstrated on laser-induced release of encapsulated material from polyelectrolyte multilayer capsules inside living cells. Metal nanoparticles were incorporated inside the walls of the capsules, and served as energy-absorbing centers for illumination by laser light. Fluorescently labeled dextran was successfully incorporated into the capsules using the heat-shrinking method. The capsules obtained by such a method exhibit improved mechanical stability being important for the delivery of encapsulated material. Upon illumination by laser light, the encapsulated dextran leaves the interior of a capsule inside a living cancer cell. Capsules not internalized by the cells are pushed up by the laser and move away from the field of view upon laser illumination from the bottom (**Fig. 3**) **[4]**. This study serves as a significant step toward the use of polyelectrolyte multilayer capsules for the delivery of medicine into bio-logical cells, and is, therefore, relevant to research on drug delivery.

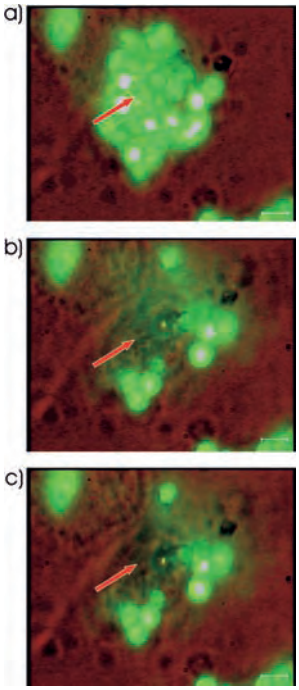


Fig. 3: Fluorescence images demonstrating the lifting up of noninternalized capsules located on top of a living MDA-MB-435S cell above and away from the imaging plane or the focus a) before, b) during, and c) after the laser beam illuminated the chamber from the bottom. The capsules were lifted up with a laser power of 50 mW. The red arrows indicate the locations of the capsules that were lifted up. The scale bars in all images correspond to 5 mm.

To mimic natural processes porphyrin nanotubes have been grown on microcapsules with well-defined thickness and length **[5]**. The tubes protrude from the capsule surface in an organized radial manner. These results suggest that an organized system of nanotubes and capsules can be obtained by using a simple method. Such porphyrin nanotubes can act as optical waveguides to propagate luminescence from one end of the tube to the capsule wall or interior; meanwhile, the capsule wall/interior can be suitably modified to utilize this energy. Hence, such a nanotube/microcapsule system should be able to mimic the architecture of chlorosomes, which are light-harvesting complexes in green photosynthetic bacteria.

G.B. Sukhorukov, O. Kreft, A. Skirtach, A.G. Shchukin, C. Déjugnat, S. Sadasivan, D.V. Andreeva, D.A. Gorin, Volodkin, D. Halozan, M. Prevot, K. Köhler, T. Mauser, A. Günther, T. Borodina, D. Radzyuk, M. Bédard, A. Praast.
g.sukhorukov@qmul.ac.uk

References:

[1] Köhler, K., Shchukin, D.G., Möhwald, H., Sukhorukov, G.B. Thermal Behavior of Polyelectrolyte Multilayer Microcapsules. 1. The Effect of Odd and Even Layer Number. J. Phys. Chem. B, **109**, 18250-18259 (2005).

[2] Mauser, T.; Dejugnat, C.; Sukhorukov, G. B. Balance of Hydrophobic and Electrostatic Forces in the pH Response of Weak Polyelectrolyte Capsules. J. Phys. Chem. B., **110** (41), 20246-20253. (2006).

[3] Andreeva, D.V., Gorin, D.A., Shchukin, D.G., Sukhorukov, G.B. Magnetic Microcapsules with Low Permeable Polypyrrole Skin Layer. Macromol. Rapid Commun., **27** (12) 931-936 (2006).

[4] Skirtach, A.G., Muñoz Javier, A., Kreft, O., Köhler, K., Piera Alberola, A., Möhwald, H., Parak, W.J., Sukhorukov, G.B. Laser-Induced Release of Encapsulated Materials inside Living Cells. Angewandte Chemie Intern. Ed., **45**, 4612-4617 (2006).

[5] Sadasivan, S., Köhler, K., Sukhorukov, G.B. Fabrication of Organized Porphyrin-Nanotube-Attached Heat-Sensitive Polyelectrolyte Capsules. Advanced Functional Materials, **16** (16), 2083-2088 (2006).

Ordering of Functionalized Nanoparticles

Dayang Wang 29.03.1972
1993: B. Eng. Chemistry (Jilin University, China)
Thesis: Synthesis and characterization of side-chain liquid crystalline poly(6-[4-(p-nitrophenyl)azo]phenoxy-1-hexyloxy maleic acid monoester).
1998: PhD, Chemistry (Jilin University, China)
Thesis: Polymer-directed synthesis of inorganic nanoparticles for high density information processing and storage.
1999: Postdoctoral Fellow (Dept. Mech. Eng., Hong Kong University of Science and Technology, Hong Kong)
2000-2003: Postdoctoral Fellow (Max Planck Institute of Colloids and Interfaces, Potsdam)
2001: Alexander von Humboldt Research Fellow (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2003: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

The self-assembly of colloidal particles allows for the construction of highly ordered structures on all length scales and for modeling the interactions between particles. Self-assembly is the hallmark of supramolecular chemistry, in which molecular components are spontaneously organized via covalent or non-covalent interactions into hierarchical structures having the complexity of the structures observed in nature. Compared with dazzlingly diverse supramolecules, the self-assembly of colloidal particles is rather simple. This simplicity arises primarily from the fact that the surface chemistry of colloidal particles is isotropic, leading to isotropic interaction between the particles. There is therefore little control over the spatial association between the particles. To circumvent this challenge, colloidal particles need to be imparted with the same moments of anisotropic interaction, or "valences" as atoms and molecules. In this way colloidal particles can be directed to organize by design **[1]**. Accordingly, the objective of our research activities is to fabricate new functional particles or to patch particles with new surface functionalities so as to fabricate colloidal "atoms" or "molecules". We therefore aim to translate the language of molecular and supramolecular chemistry to govern the integration of colloidal particles in a spatially and temporally controlled manner.

A. Interfacial Self Assembly of Nanoparticles

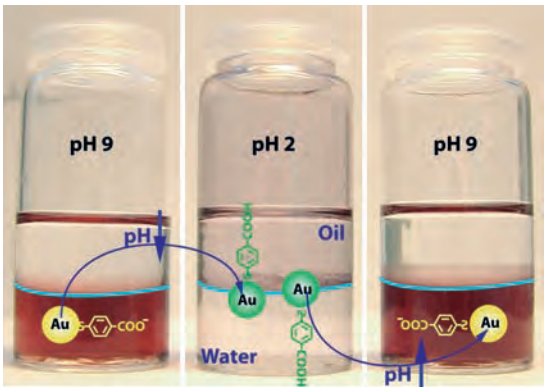


Fig. 1: pH-responsive interfacial self-assembly of aqueous 6 nm gold nanoparticles, stabilized by mercaptobenzoic acid. In the glass vial, the bottom phase is water and the top phase is heptane.

The unique characteristic of self-assembly encountered in nature is that it is dynamic, (i.e. assembly and disassembly occurs in a controlled manner). Contrastingly, the self-assembly of colloidal crystals is static and once the particles are associated, they can not be induced to dissociate. Using the water-oil interface as a platform for the self-assembly of charged hydrophilic nanoparticles, we have demonstrated that these assemblies exhibit characteristics of dynamic self-assembly **[2]**. Decreasing the surface charge density of charged nanoparticles results in an increase of their surface hydrophobicity, leading to the spontaneous assembly of those particles at the interface. If the particles were smaller than 15 nm, electrostatic repulsion between the particles, due to an increase in their surface charge density, was sufficient to redisperse the particles and pull them back to the bulk water phase (**Fig.1**). The reversibility of the interfacial assembly of nanoparticles may be due to the fact that the interfacial attachment energy of particles of a size less than 15nm is comparable to the thermal energy of those particles, resulting in a high sensitivity to energy variations of the system. The switchable surface wettability of the nanoparticles is central to their success as dynamically self-assembling materials.

The interface between water and oil provides a unique two-sided platform that enables a combination of chemistry in the aqueous and organic phases to be employed. Specific interactions, such as inclusion between a cyclodextrin and adamantine, and DNA-base pairing were used to direct nanoparticles to self-assemble at water/oil interfaces. Subsequently the surface chemistry of the particles was altered to deposit different nanoparticles onto the interface and form a heterogeneous structure with respect to both sides of the interface **[3]**.

B. Facet-Selective Growth and Organization of Nanoparticles

Additionally, different facets of nanoparticles may be used to direct the spatial association of those particles. To achieve the facet-selective self-assembly of colloidal particles, the

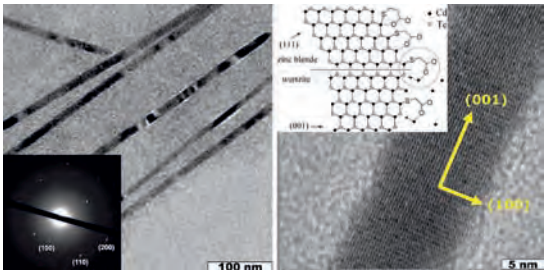


Fig. 2: Aqueous wurtzite CdTe nanorods derived from secondary coordination of thioglycolic acid.

different facets should be well defined and spatially segregated on the particles. In this context, non-spherical shapes are ideal. Recently, we systematically explored the influence of various experimental variables such as temperature, stabilizer chemistry, precursor concentration, and pH on the growth of semiconductor nanocrystals in aqueous media **[4]**. Due to the interaction between different ligands, colloidally stable one dimensional (1D) CdTe nanostructures such as nanorods and nanowires were successfully fabricated, providing building blocks for facet-selective self-assembly (**Fig.2**).

C. Stereo-Decoration of Au Nanodots on Micro-Spheres

To transform colloidal particles into colloidal "atoms" or "molecules", a straightforward but challenging way is to pattern the particle surfaces. However, conventional lithographic techniques only pattern planar surfaces due to the lack of appropriate masks for highly curved surfaces. We recently succeeded in developing a colloidal lithographic method that uses the interstitial gaps in the upper layers of colloidal crystals as masks for depositing Au vapor onto spheres in the lower layers **[5]**. Using anisotropic reactive ion etching and azimuthally offset vapor deposition, well-controlled numbers of Au nanodots were selectively deposited on different regions of the microspheres (**Fig.3**). The number of Au dots was determined by the structure of the colloidal crystal template, the size of the template spheres and experimental variables such as the etching time and the incident angle of the Au vapor. The spatial arrangement of the Au dots on the microspheres resembled the configuration of hybridized orbitals of carbon or silicon atoms. In this scenario, Au dots can be employed as "valences" to direct the spatial association of microspheres. This could pave a new way – colloidal valence chemistry– to organize colloidal particles into hierarchical structures with the complexity inherent in molecules or supramolecules.

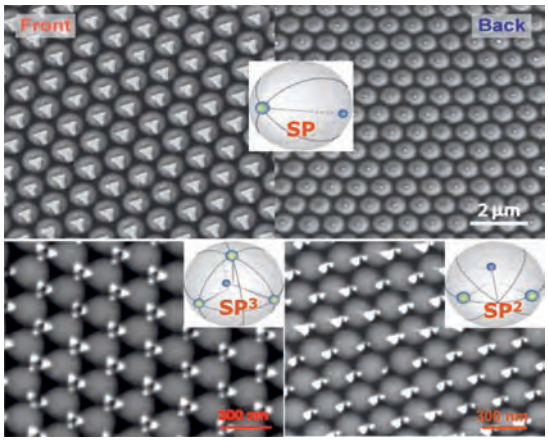


Fig. 3: Polystyrene microspheres decorated with 2, 3, and 4 Au nanodots, having spatial arrangements that are reminiscent of the hybridized orbitals of carbon atoms.

D. Wang, M. Chanana, E. Edwards, K. Li, W. Li, F. Reincke, J. Wang, G. Zhang, H. Zhang.
dayang.wang@mpikg.mpg.de

References:

[1] Zhang, H., Edwards, E., Wang, D., Möhwald, H.: Directing Self-Assembly of Nanocrsytals beyond Colloidal Crystallization, Phys. Chem. Chem. Phys. **8**, 3288-3299 (2006).

[2] Reincke, F., Kegel, W., Zhang, H., Nolte, M., Wang, D., Vanmaekelbergh, D., Möhwald, H., Understanding the Self-Assembly of Charged Nanoparticles at the Water/Oil Interface Phys. Chem. Chem. Phys. **8**, 3828-3825 (2006).

[3] Wang, J., Wang, D., Sobal, N., Giersig, M., Jiang, M., Möhwald, H., Stepwise Directing Nanocrystals to Self-Assemble at Water/Oil Interfaces Angew. Chem. Int. Ed. **45**, 7963-7966 (2006).

[4] Zhang, H., Wang, D., Yang, B., Möhwald, H., Manipulation of Aqueous Growth of CdTe Nanocrystals to Fabricate Colloidally Stable One-Dimensional Nanostructures. J. Am. Soc. Chem. **128**, 10171-10180 (2006).

[5] Zhang, G., Wang, D., Möhwald, H., Decoration of Au Nanodots on Microspheres – Giving Colloidal Spheres Valences Angew. Chem. Int. Ed. **44**, 7767-7770 (2005).

INTERNATIONAL JOINT LABORATORY

Molecular Assemblies of Biomimetic Systems and Nanostructures

Junbai Li 01.12.1964

1989: Diploma, Chemistry (Jilin University, China) Thesis: Photon Correlation Spectroscopy Investigation of Ultrafine Polymer Particles

1992: PhD, Chemistry (Jilin University, Mainz University) Thesis: Homodyne Correlation Spectroscopy of Macromolecular Ultrafine Particle in Solution and Dynamic Light Scattering of Thermally Excited Capillary Waves on a Liquid Surface

1993: Postdoc (Foundation of Research and Technology, Hellas)

1994-1996: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)

1996: Full Professor (International Joint Lab, Institute of Photographic Chemistry, Chinese Academy of Sciences)

Since 1999: Full Professor (International Joint Lab, Institute of Chemistry, Chinese Academy of Sciences)

Aims

• Molecular assemblies of biomimetic systems: Membrane hydrolysis; Complex assembly of lipids, proteins, enzymes and biomolecular motors: F_0F_1, Kinesin, Actin; Biogenic microcapsules; Self assembly and in vitro characterization of biological molecules such as DNA, peptide and single cells as well as their mixtures with surfactant and polymers.

• Bio-interfaces: molecular patterns, surface modification, molecular recognition of enzymes, chemical recognition at cell surfaces, transport through cell membranes.

• Design and synthesis of bioinspired molecules and materials for drug release and gene delivery.

• Nanostructures: Design, synthesis, characterization and functionalization of nanoparticles, nanopatterns, nanotubes, nanocrystals.

Results

A. Molecular Assembly of Biomimetic Systems

• ATPase Assembled into Microcapsules for ATP Biosynthesis

The biomolecular motor, ATPase assembled in lipid-modified polyelectrolyte microcapsules enables to use the process of ATP biosynthesis as a novel routine to fabricate bionanodevices. This assembled complex can not only help us to understand the biological function of ATPase molecules but also provides a well-defined container for the storage of energy currency as an artificially designed system containing ATPase. When vital activities need energy, ATP will be released across the wall of the capsules as power supply (**Fig. 1**).

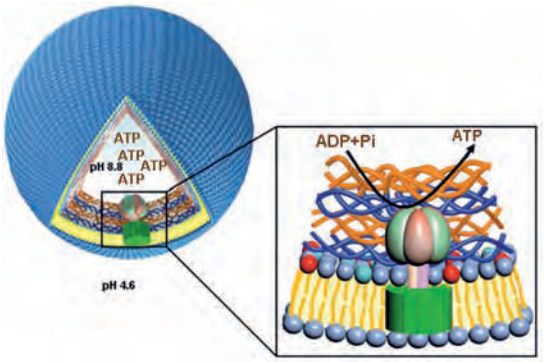


Fig. 1: Schematic representation of the arrangement of CFoF1-ATPase in lipid-coated microcapsules

• Assembled Peptide Vesicles for Gene Delivery and Release in Cells

The synthesized multivalent cationic peptide-lipid (MCPL) is considered for DNA delivery to mammalian cells. The MCPL can form dispersed liposomes. The binding of MCPL liposomes with DNA can be detected by a standard ethidium bromide (EtBr)-DNA fluorescence quenching assay. As such assembled DNA/EtBr/MCPL solution is incubated with trypsin. The fluorescence intensity increases after trypsin hydrolyzed the head-group of MCPL suggests the DNA release from the complexes. The high enhanced transfecting efficiency of MCPL with DNA is expected. We intend to design and synthesize several different types of cationic peptides for this purpose (**Fig. 2**).

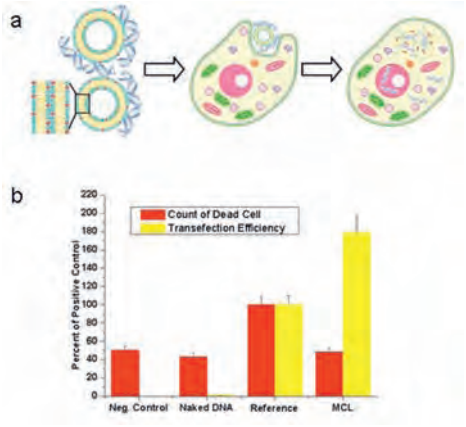


Fig. 2: (a) Schematic illustration of DNA release from cationic lipopeptide vesicles; (b) Gene transfection efficiency and cytotoxicity results after 48 h in HeLa cells

• Conversion of Dipeptide for Gene Delivery through the Cell Membrane

Positively charged dipeptides can self-assemble spontaneously into the structure of vesicles under a certain condition. Such a conversion could readily bring genes into cells through the membrane. The self-assembly behavior of dipeptide nanostructure can be exploited as a new class of molecular transporter for the delivery of a wide range of foreign substances such as drugs and proteins. We are interested in investigating the conversion process quantitatively and building up models. Several relevant systems will be developed (**Fig. 3**).

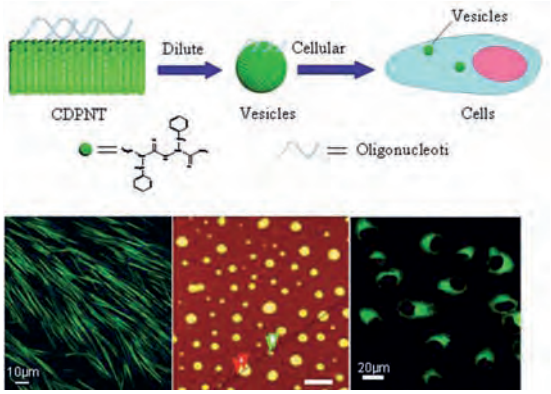


Fig. 3: Proposed mechanism of transition of the CDPNTs into vesicles for oligonucleotide delivery and corresponding microscopic results.

B. Nanostructures

• *Protein Supported Lipid Patterns for the Targeted Recognition*

Supported lipid micro-, nanopatterns are one of the most popular biomembrane models which can be applied to fundamental studies of cell membrane science and the engineering of integrated lipid membrane microdevices. Our aim is to fabricate stable lipid bilayer patterns to create the possibility of cooperating specific components like channels or receptors for specific recognition, which allows transferring materials (like drugs) to a solid surface for the medical application.

• *Template Synthesized Polymer Nanotubes*

Most synthesized nanotubes exhibit a good perspective for application in the biological or medical field, for instance for bioseparations or materials transport. At this stage, precisely controlling the inner diameter and biocompatibility of the synthesized nanotubes is highly required. Template synthesized polymer nanotubes have the obvious features of high flexibility and mechanical stability. With the combination of self-assembly and layer-by-layer assembly techniques one can modify the inner pores in different way through electrostatic absorption, covalent bond, hydrogen bond or chemical reaction to obtain micro-nanosize tubes. The achieved nanotubes may contain the features of biocompatibility, luminescence, biodegradability or thermosensitivity, which promises the potential applications in polar cells, drug delivery, biocatalysis or tissue engineering (**Fig. 4**).

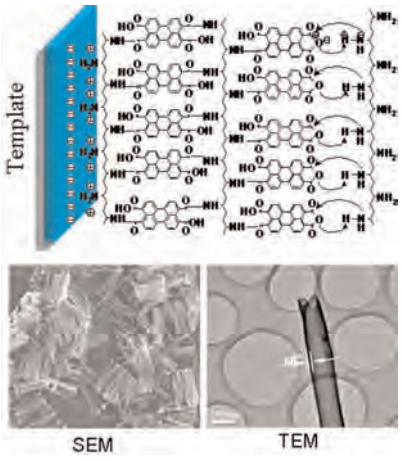


Fig. 4: SEM and TEM images of assembled multi-functional composite nanotubes via covalent bond

• *Decoration of Gold Nanoparticles*

The nanocomposites of gold nanoparticle (AuNPs) with various macromolecules display much potential applications in the fields of biology and nanotechnology. Surface-initiated atom-transfer radical polymerization on the AuNP surface provides a perfect core-shell nanostructure and will alter the property of nanoparticles and response to interface and environment. Such nanosized hybrids are considered for delivery of biomolecules, catalysts or drugs (**Fig. 5**).

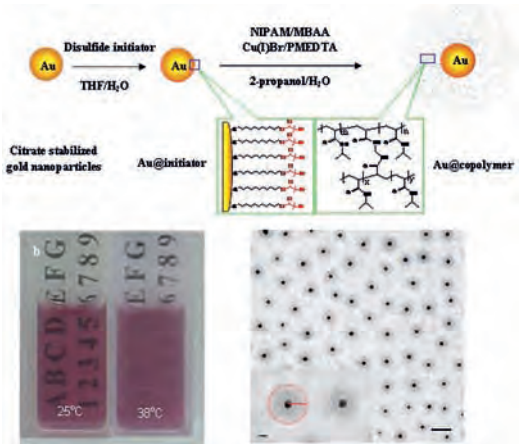


Fig. 5 (a) Scheme of the preparation of Au@PNIPAM nanoparticles by the ATRP procedure; (b) Optical photos of Au@copolymer hybrids with 1% MBAA at 25 and 38°C, respectively.; (c) TEM image of Au@copolymer hybrids with 1% MBAA to encapsulate 3.5 nm gold nanoparticles. Scale bar = 20 nm.

J.B. Li, G.C. Cui, Q. He, Y. Cui, S.F. Ai, W.X. Song, D.X. Li, Y. Tian, X.M. Zhang, L. Duan, X.H. Yan, Y. Yang, K.W. Wang, W. Qi, J.B. Fei, D.Y Hua;
Collaborated with MPI: G. Brezesinski, H. Möhwald.
Junbai.Li@mpikg.mpg.de

References:

[1] Tian, Y., He, Q., Cui, Y., Li, J.: Fabrication of Protein Nanotubes Based on Layer-by-Layer Assembly. Biomacromolecules **7**, 2539-2542 (2006).

[2] Tian, Y., He, Q., Tao, C., Li, J.: Fabrication of Fluorescent Nanotubes Basel on Layer-by-Layer Assembly via Covalent Bond. Langmuir **22** 360-362 (2006).

[3] Cui, Y., Tao, C., Tian, Y., He, Q., Li, J.: Synthesis of PNIPAM-co-MBAA Copolymer Nanotubes with Composite Control. Langmuir **22**, 8205-8208 (2006).

[4] Ai, S., He, Q., Tao, C., Zheng, S., Li, J.: Conductive Polypyrrole and Poly(allylamine hydrochloride) Nanotubes Fabricated with Layer-by-Layer Assembly. Macromol. Rapid Commun. **26**, 1965-1969 (2005).

[5] Cui, Y., Tao, C., Zheng, S., He, Q., Ai, S., Li, J.: Synthesis of Thermosensitive PNIPAM-co-MBAA Nanotubes by Atom Transfer Radical Polymerization within a Porous Membrane. Macromol. Rapid Commun. **26**, 1552-1556 (2005).

[6] Li, J, Möhwald, H., An, Z., Lu, G.: Molecular Assembly of Biomimetic Microcapsules. Soft Matter **1**, 259-264 (2005).

[7] Wang, X., Zheng, S., He, Q., Brezesinski, G., Möhwald, H., Li, J.: Hydrolysis Reaction Analysis of L-Alpha-Distearoylphosphatidyleholine Monolayer Catalyzed by Phospholipase A(2) with Polarization-Modulated Infrared Reflection Absorption Spectroscopy. Langmuir **21**, 1051-1054 (2005).

[8] Zhai, X., Bartel, M., Brezesinski, G., Rattay, B., Möhwald, H., Li, J.: Small Angle X-Ray Scattering (SAXS) and Differential Scanning Calorimetry (DSC) Studies of Amide Phospholipid. Chem. Phys. Lipids **133**, 79-88 (2005).

Hybrid MPG/FhG Research Group "Nanotechnology for Life Science" & Golm Campus Initiative "Bioactive Surfaces"

Jean-François Lutz 08.01.1972
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 2004: Group Leader (Fraunhofer Institute for Applied Polymer Research, Potsdam)

Within the last few years, the Max-Planck society and the Fraunhofer society have established a successful collaboration program in the science park of Golm. Such joint collaboration MPG/FhG is almost unique in Germany and combines the complementary skills of both institutions (i.e. fundamental and applied research) for developing novel generations of applied materials.

The first initiative was the creation in April 2002 of the group "Nanotechnology for Life Science", a hybrid research team between the Fraunhofer Institute for Applied Polymer Research (IAP) and the Max Planck Institute of Colloids and Interfaces. The team is currently lead by Dr. Jean-François Lutz and combines fundamental research and applied projects with industrial partners (e.g. Schering A.G., Qiagen GmbH, Capsulution). For instance, the team focuses principally on potential applications of macromolecules in all aspects of human medicine (delivery, diagnostics, biomaterials). A first objective is to prepare at the molecular level novel macromolecules with a life science potential, such as water soluble polymers, amphiphilic copolymers, biodegradable polymers, polymer bioconjugates or stimuli responsive polymers. For reaching this goal, several modern methods of synthesis such as controlled radical polymerization, living polymerization of polypeptides, ring opening polymerization or click chemistry are combined **[1-4]**. 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) and unprecedented properties. A good example of such synthetic work is the recent design of thermoresponsive polymers based on biocompatible oligo(ethylene glycol) segments **[5,6]**. The stimuli-responsive behavior of these new polymers can be precisely controlled by simply varying their molecular structure. Moreover, in comparison to standard thermoresponsive polymers (e.g. PNIPAM) these novel structures possess the advantage to exhibit a reversible phase transition. Such "smart" and biocompatible macromolecules possess a very high potential for bio-applications.

Besides applied polymer chemistry, the group "Nanotechnology for Life Science" focuses intensively on nanomaterials design. The team develop tailor-made 2D (functional surfaces) or 3D (nanoparticles) nanostructures for a large range of medical applications such as bioseparation, controlled drug delivery, non-viral gene delivery or magnetic resonance imaging. Various types of colloidal nanostructures were prepared and studied during the last few years such as nano-aggregates capable to transport DNA into living cells (polyplexes), microgels utilizable for controlled drug delivery, stealth-nanoparticles, which can be used in several aspects of nanobiotechnology, and micellar assemblies (micelles, vesicles), which possess an enormous applicative potential as nanocontainers for drug delivery **[7-10]**.

The success of the "Nanotechnology for Life Science" initiative confirmed the complementary roles of Fraunhofer, Max-Planck Institutes and University Potsdam within the Research Campus Golm. Thus in 2007, this dual collaboration will be transformed into a bigger campus network "Bioactive Surfaces" sponsored by both Fraunhofer and Max Planck Societies. The goal of this new project is to create a strong local research force for developing novel generations of bioactive surfaces (i.e. colloidal or flat model surfaces) capable of interacting "on demand" with biological systems such as DNA, proteins, enzymes or cells. **Fig. 1** summarizes the scientific strategy of this research program. The main scientific objectives are both fundamental and applied. This project is designed for studying the fundamental aspects of bioactive surfaces and moreover for transforming this basic knowledge into marketable applications. In that regard, the proposed cooperation between Max Planck Institutes and Fraunhofer Institutes is ideal.

References:
[1] J.-F. Lutz, 1,3-Dipolar Cycloadditions of Azides and Alkynes: A Universal Ligation Tool in Polymer and Materials Science, Angew. Chem. Int. Ed., early view (2007).
[2] J.-F. Lutz, H. G. Börner, K. Weichenhan, Combining ATRP and "Click" Chemistry: a Promising Platform toward Functional Biocompatible Polymers and Polymer Bioconjugates, Macromolecules, **39**, 6376-6383 (2006).
[3] J.-F. Lutz, H. G. Börner, K. Weichenhan, Combining ATRP and Click Chemistry: a Versatile Method for Preparing End-Functional Polymers., Macromol. Rapid Commun., **26**, 514-518 (2005).

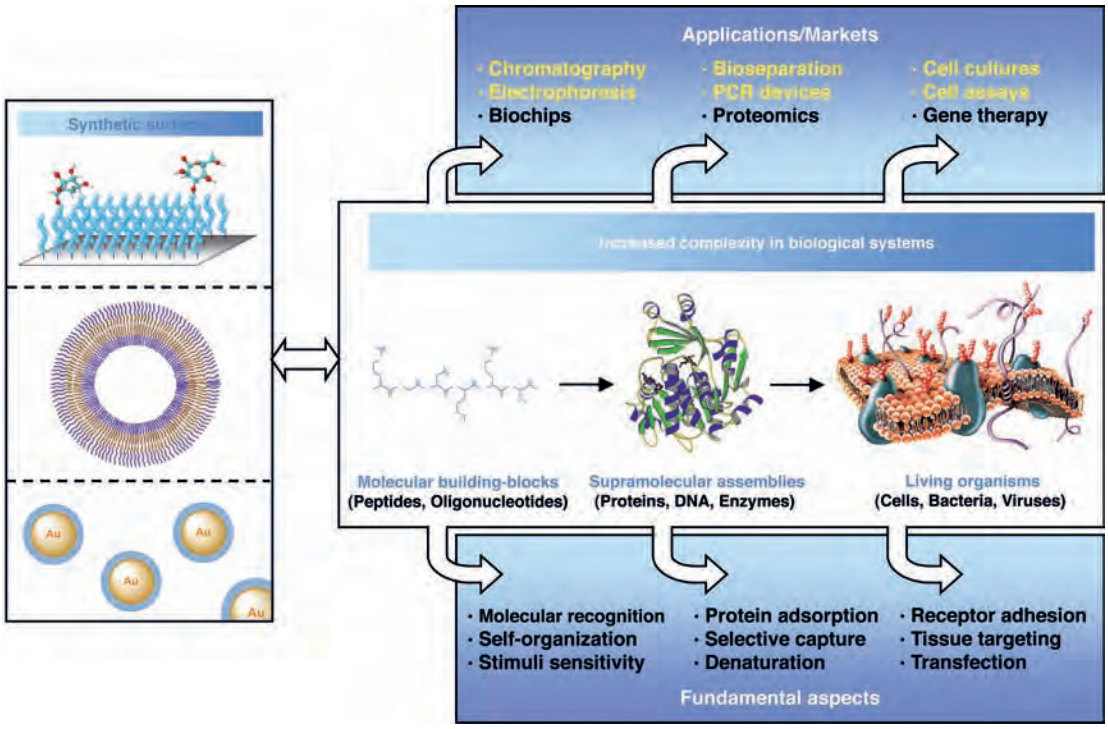


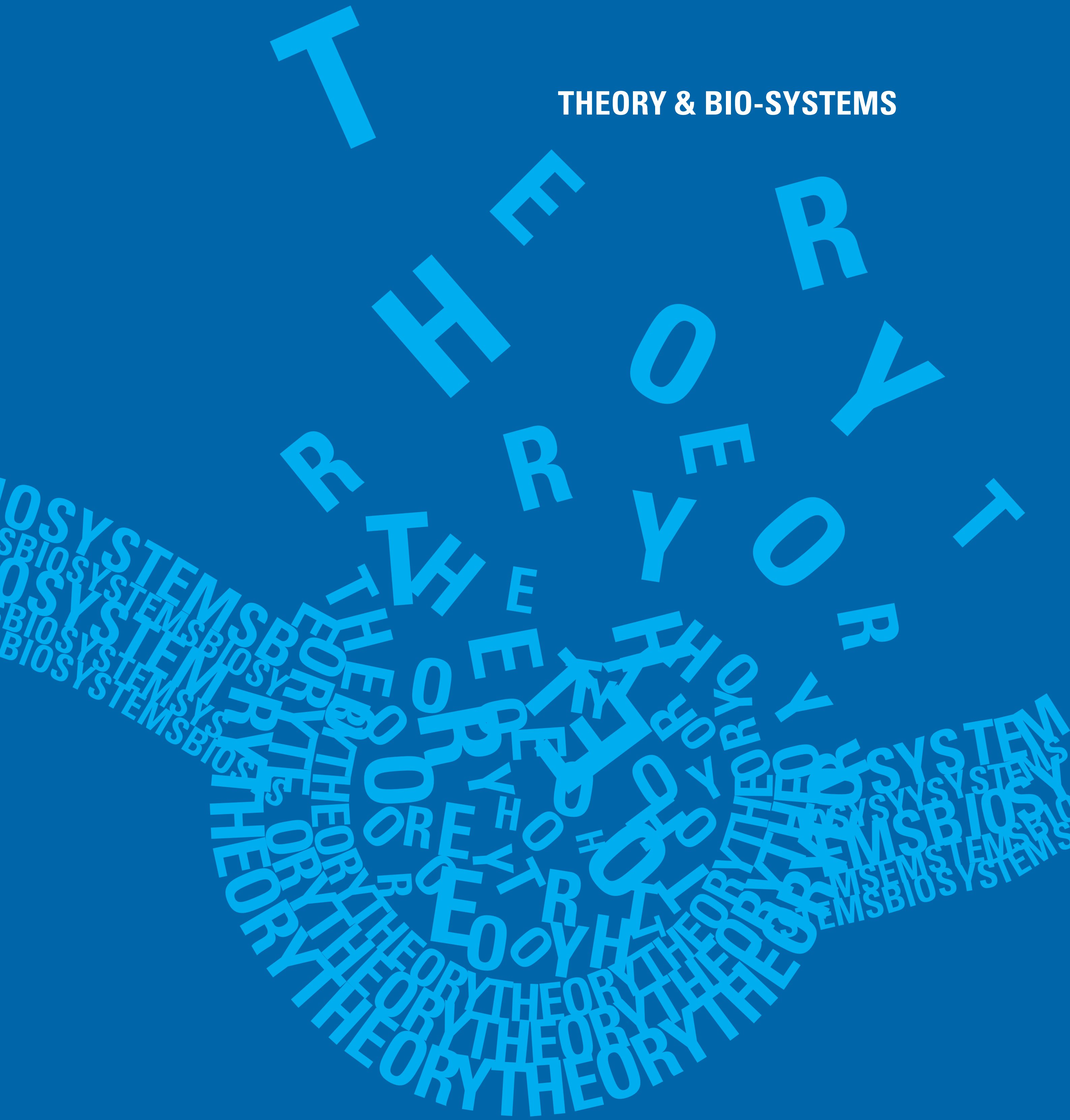
Fig. 1: Schematic description of the main fundamental and applied issues of the campus project "Bioactive Surfaces". The left part of the graphic represents examples of flat or colloidal synthetic model surfaces. The right part of the graphic lists the biological systems, which will be investigated in this program. The applications highlighted in yellow will be principally studied within the time frame of the campus project.

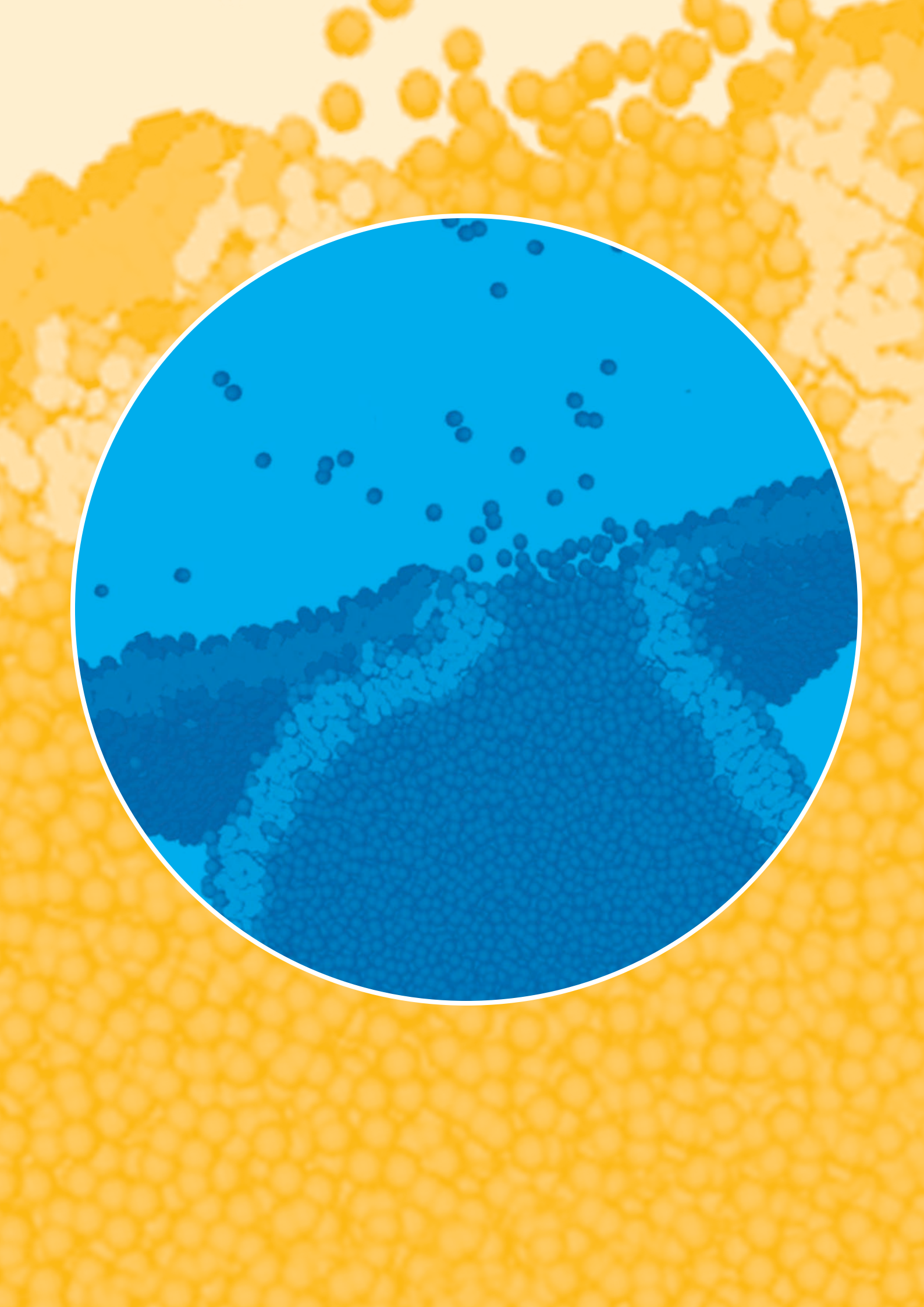
Three main scientific aspects will be explored in this project: (a) The development of specific interactions between synthetic surfaces and biological systems. (b) The control of conformational variations using artificial surfaces. (c) The preparation of stimuli-sensitive surfaces capable of interacting "on demand" with biological systems. For solving such complex scientific issues, a multidisciplinary network is indeed necessary. Thus, this project combines all the complementary competences present in the Science-Park Golm: theory, polymer chemistry, biochemistry, colloidal physico-chemistry, physics of interfaces, biology and applied biotechnology. More precisely, this novel interdisciplinary network will involve active collaborations between the Fraunhofer Institute for Applied Polymer Research (Research group Nanotechnology for Life Science), the Fraunhofer Institute for Biomedical Engineering (IBMT), the Max Planck Institute of Colloids and Interfaces (theory, colloids and interfaces departments) and the Institute of Physical Biochemistry of the University of Potsdam.

J.F. Lutz, S. Pfeifer, O. Akdemir, M. Chanana, A. Hoth.
lutz@iap.fhg.de

[5] J.-F. Lutz, A. Hoth, Preparation of Ideal PEG Analogues with a Tunable Thermosensitivity by Controlled Radical Copolymerization of 2-(2-methoxyethoxy)ethyl Methacrylate and Oligo(ethylene glycol) Methacrylate, Macromolecules, **39**, 893-896 (2006).
[6] J.-F. Lutz, O. Akdemir, A. Hoth, Point by Point Comparison of Two Thermosensitive Polymers Exhibiting a Similar LCST: Is the Age of Poly(NIPAM) Over? J. Am. Chem. Soc., **128**, 13046-13047 (2006).
[7] S. Kubowicz, J.-F. Baussard, J.-F. Lutz, A. F. Thünemann, H. von Berlepsch, A. Laschewsky, Observation of Multicompartment Micelles Formed via Self-Assembly of Linear ABC Triblock Copolymers in Aqueous Medium, Angew. Chem. Int. Ed., **44**, 5262-5265 (2005).
[8] J.-F. Lutz, A. F. Thünemann, K. Rurack, DNA-like "Melting" of Adenine- and Thymine-functionalized Synthetic Copolymers, Macromolecules, **38**, 9556-9563 (2005).
[9] J.-F. Lutz, S. Pfeifer, M. Chanana, A. F. Thünemann, R. Bienert, H-bonding Directed Self-Assembly of Synthetic Copolymers Containing Nucleobases: Organization and Colloidal Fusion in a Non-competitive Solvent., Langmuir, **22**, 7411-7415 (2006).
[10] J.-F. Lutz, S. Stiller, A. Hoth, L. Kaufner, U. Pison, R. Cartier, One-Pot Synthesis of PEGylated Ultrasmall Iron-Oxide Nanoparticles and Their in Vivo Evaluation as Magnetic Resonance Imaging Contrast Agents, Biomacromolecules, **7**, 3132-3138 (2006).

THEORY & BIO-SYSTEMS





Research in the Department of Theory & Bio-Systems

So einfach wie möglich, aber nicht einfacher
Albert Einstein

The researchers and doctoral students of the Department of Theory and Bio-Systems form one experimental and six 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; until 2005);
- *Volker Knecht* (theory; proteins and membranes; since 2006).
- *Christian Seidel* (theory, polymers and polyelectrolytes);
- *Julian Shillcock* (theory, supramolecular modelling; until 2005);
- *Thomas Weikl* (theory, proteins and membranes).

The Theory and Bio-Systems Department is responsible for and coordinates the International Max Planck Research School on "Biomimetic Systems", the European Early Stage Training Network about the same topic, in which three departments of the MPI participate, and the European Research Network on "Active Biomimetic Systems". The management of these networks is done by *Angelo Valleriani*.

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

Systems

Our research is focused on bio-systems, which represents an abbreviation for "biomimetic and biological systems". If one looks at these systems bottom-up, i.e., from small to large length scales, one encounters a hierarchy of such systems including

- polymers and proteins,
- molecular motors,
- rods and filaments,
- membranes and vesicles, and
- networks in bio-systems.

When these systems are approached top-down, i.e., from larger to smaller scales, one encounters the problem of restricted geometries or confining walls and interfaces. In general, interfaces may be used to suspend and organize smaller bio-systems in order to make them accessible to systematic studies.

Phenomena

During the last two years, specific phenomena addressed in the area of polymers and proteins included the conformation of peptides at interfaces, the process of protein folding, and dense brushes of polyelectrolytes. As far as motor proteins or molecular motors are concerned, we studied the chemomechanical coupling of single motors and the cooperative transport by several such motors, see **Fig. 1**.

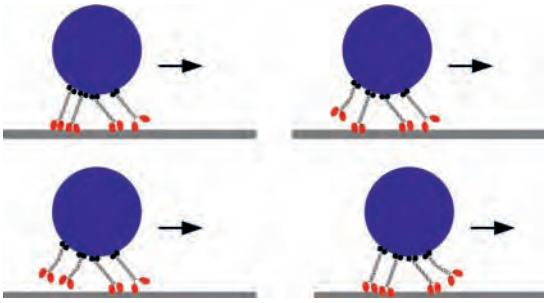


Fig. 1: Cooperative transport of cargo by several molecular motors

The cooperative behavior of rods and filaments provides many unusual phenomena such as the active polymerization of filaments, the ordering of filaments on substrate surfaces covered with immobilized molecular motors, see **Fig. 2**, and ordered mesophases of rods with adhesive endgroups.

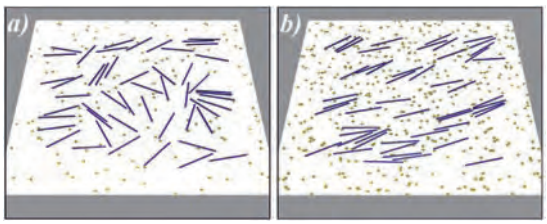
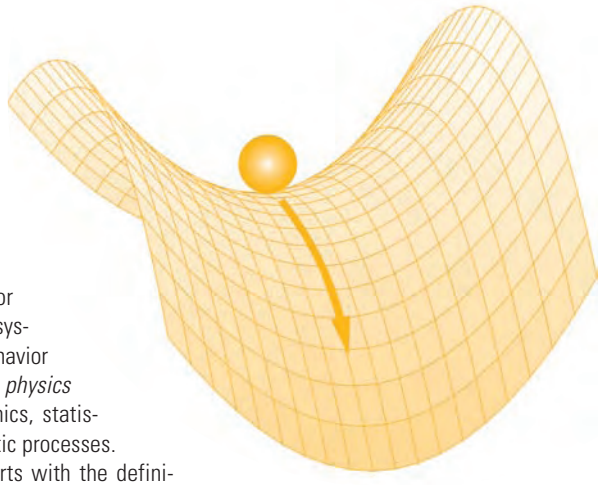


Fig. 2: (a) Disordered and (b) Ordered nematic states of rod-like filaments (blue) on a substrate surface with immobilized molecular motors (yellow spots). The transition from (a) to (b) is induced by an increase in the motor density.

In the research field of membranes and vesicles, we have improved our theoretical models for membrane fusion and membrane adhesion. A timely topic is the adhesion of membranes via specific molecular bonds, see **Fig.3**. In addition, the direct imaging of intramembrane domains and vesicle fusion has been further developed, see **Fig. 4**.



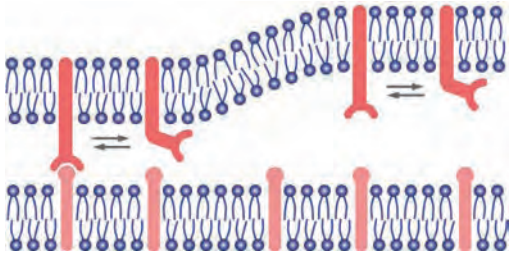


Fig. 3: Adhesion of two membranes via active receptors or stickers that can attain both an adhesive and a non-adhesive state.

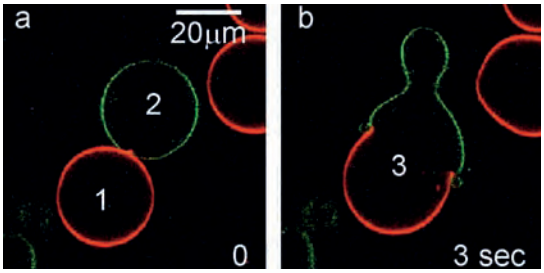


Fig. 4: Fusion of giant vesicles as observed by fluorescence microscopy. The two colors (red and green) correspond to two different membrane compositions that form stable domains after the fusion process has been completed.

Bio-systems are quite complex and exhibit many levels of self-organization. One rather general framework for these systems is provided by network models. During the last two years, we have worked on networks of motor cycles, activity pattern on scale-free networks, and network models for biological evolution.

All systems and phenomena that have been mentioned in this overview will be covered in more detail on the following pages.

Methods

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.

Our 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 our 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; lattice models for transport by molecular motors; Markov models for cooperative motor transport as well as network models for motor cycles.

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.

Several types of computer simulations are applied and further developed: Molecular Dynamics, Dissipative Particle Dynamics, and Monte Carlo methods. Molecular Dynamics is used for particle based models of supra-molecular assemblies; Dissipative Particle Dynamics, which is a relatively new simulation algorithm, is useful in order to extend the Molecular Dynamics Studies towards 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. This lab is also responsible for the advanced confocal microscope that is available to all four departments of the MPI.

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

Reinhard Lipowsky
Director of the Department of Theory & Bio-Systems

Peptide Folding, Aggregation, and Adsorption at Interfaces

Volker Knecht 06.01.1970
1996: Diploma in physics (University of Kaiserslautern)
Thesis: Computer based renormalization group study of the two-dimensional XY model
1997: Software trainee (TECMATH GmbH, Kaiserslautern)
1998-1999: Software engineer (LMS Durability Technologies GmbH, Kaiserslautern)
2003: PhD, Physics (MPI of biophysical chemistry, Göttingen)
Thesis: Mechanical coupling via the membrane fusion SNARE protein syntaxin 1A: a molecular dynamics study
2003-2005: Postdoc (University of Groningen, the Netherlands)
2005-2006: Postdoc (MPI of Colloids and Interfaces, Potsdam)
Since 2006: Group Leader (MPI of Colloids and Interfaces, Potsdam)

A number of neurodegenerative diseases such as Alzheimer's or Parkinson's are related to the precipitation of protein into β-sheet rich amyloid fibrils. The transformation of a protein from the functional soluble state to the pathogenic fibril state is believed to be initiated by a misfolding of the protein and the formation of small oligomers. Interfaces can promote or inhibit fibril formation depending on the amino acid sequence of a peptide and the molecular structure of the interface. To study the early steps of fibril formation in atomic detail experimentally is difficult due to the tendency of misfolded proteins to aggregate and the short lifetimes of small oligomers. Computer simulations therefore provide an indispensable tool to study these processes.

We employ molecular dynamics simulations to study fibril forming peptides in solution and at interfaces as model systems. In our simulations, peptide(s) and solvent environment are described in atomic detail. Atoms are modeled as classical point masses whose interaction is described using a semi-empirical force field. The simulations provide a high spatial and temporal resolution of biomolecular processes. However, due to their computational expense such simulations suffer from a notorious sampling problem. Therefore, experimental data are important bench-marks for the simulations. In a collaboration with the group of Gerald Brezesinski from the interfaces department, we have studied the fibrillogenic peptide B18, a fragment of the sea urchin fertilization protein Bindin and corresponding to resides 103-120 of the parent protein **[1-3]**.

In water, B18 tends to form β-strand-loop-β-strand conformations (see Fig. 1(a) *middle*). β-sheets are mainly formed by hydrophobic residues (*yellow*). In the initial steps of the adsorption at a water/vapor interface, α-helical and turn conformations are induced in the C-terminal segment which is partially hydrophilic (see **Fig. 1(a)** right) **[1]**. Upon adsorption to a (negatively charged) DPPG monolayer, B18 becomes somewhat more disordered. The effect of the environment on the peptide structure is in agreement with data from circular dichroism (CD) and infrared spectroscopy **[2]**. For the first time, we have studied the formation of partially ordered dimers of strand-loop-strand forming peptides in explicit solvent (see **Fig. 1(b)**) **[3]**. Whereas previous simulations using implicit solvation models predicted planar aggregates, we observe highly twisted β-sheet structures, indicating the twist to be (partially) a specific solvent effect.

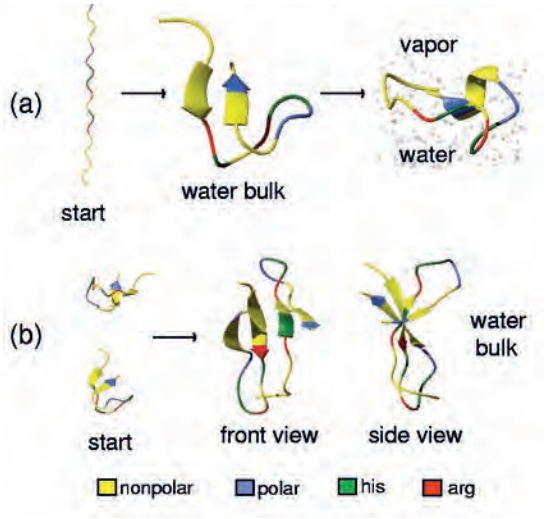


Fig. 1: Folding and aggregation of B18 peptide in different environments in molecular dynamics simulations. (a) In water, B18 tends to adopt β-strand-loop-β-strand structures (middle). Adsorption to a water/vapor interface induces α-helical conformations (right). (b) In water bulk, partially ordered β-sheet rich dimers can form on a nanosecond timescale. The peptide backbone is shown in ribbon representation, the amino acid sequence is color-coded.

In water, pre-formed α-helical conformations are partially kinetically trapped on the nanosecond timescale of our simulations at room temperature, but convert into β-sheet structures at elevated temperature as shown in **Fig. 2**. The transition is initiated by a quick hydrophobic collapse (see **Fig. 2(c,d)**). α-helical conformations dissolve into turn and coil conformations (see **Fig. 2(a,b)**) and the number of main chain hydrogen bonds decreases (see **Fig. 2(e)**). Upon formation of β-sheets (see **Fig. 2(b)**), the peptide becomes more extended again (see **Fig. 2(c)**).

A water/vapor interface stabilizes α-helical conformations in agreement with infrared data. This finding allowed the usage of a coarse grain model in which the peptide was described as a rigid helix and facilitated to study the lateral organization of multiple B18 peptide and DPPC molecules in the interface. As shown in **Fig. 3**, B18 and DPPC demix in the interface and B18 accumulates in the three-phase boundary between water, lipid, and vapor phase. At the equilibrium lateral pressure (known from experiment), the interface is fully covered by peptide and lipid molecules which remain demixed (see **Fig. 3**, right). The demixing of B18 and DPPC molecules in a water/vapor interface explains the experimental observation that adsorption of B18 to a DPPC monolayer in the liquid-expanded gas coexistence region does not change the structure of the DPPC monolayer **[1]**.

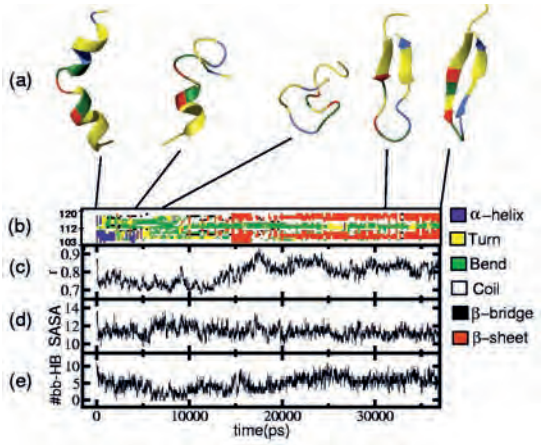


Fig. 2: α-β transition of B18 in water at elevated temperature involving a compact coil intermediate. (a) selected configurations. (b) Time evolution of the secondary structure obtained from an analysis of backbone hydrogen bonds. Here the vertical coordinate represents the residue number which is plotted against time, and the secondary structure is color-coded. (c-e) Time evolutions of (c) radius of gyration (measure of compactness of the peptide), (d) hydrophobic solvent-accessible surface area (measure of the exposure of nonpolar groups to the solvent), and (e) number of peptide main chain hydrogen bonds.

Future Work

Ongoing work is focused on (i) sequence effects on the folding and aggregation of amyloid forming peptides, (ii) membrane fusion, and (iii) electrokinetic phenomena. PhD student Madeleine Kittner who started at the beginning of January 2007 will work on peptides. Another member starting in the coming months will work on membrane fusion. A PhD student starting in February 2007 will work on a new project, (iv) modeling of molecular motors with atomic resolution. Besides these molecular dynamics studies, (v) a mesoscopic study of pore formation in membranes is carried out by the postdoc Josep Pamies.

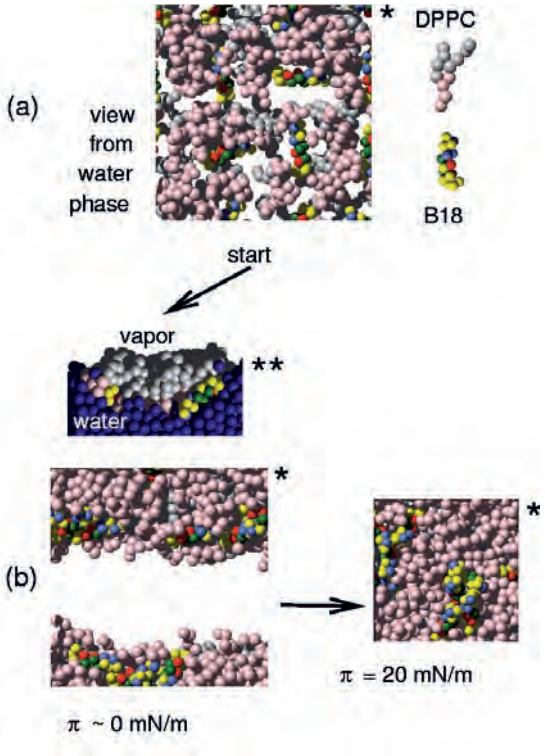


Fig. 3: Demixing of B18 peptide and DPPC lipid molecules in a water/vapor interface in simulations using a coarse grain model. (a) As initial configuration, a random distribution of molecules in the interface was used. (b, left) During a simulation peptide and lipid molecules demix spontaneously. Peptides accumulate in the three phase boundary between water, lipid, and vapor. (b, right) At the equilibrium lateral pressure (known from experiment), the interface is fully covered by peptide and lipid molecules which remain demixed. Views of configurations normal to the interface towards the vapor phase (*) or parallel to the interface (**) are shown.

V. Knecht, M. Kittner, J. Pamies
vknecht@mpikg.mpg.de

References:

[1] V. Knecht, H. Möhwald, and R. Lipowsky, Conformational diversity of the fibrillogenic fusion peptide B18 in different environments from molecular dynamics simulations, J. Phys. Chem. B, **111**, 4161-4170, 2007

[2] E. Maltseva, Model membrane interactions with ions and peptides at the air/water interface, Ph.D. thesis, Universität Potsdam (2005).

[3] V. Knecht and R. Lipowsky, Dimerization of the fibrillogenic peptide B18 in water in atomic detail, in preparation.

Protein Folding

Thomas Weikl 01.04.1970
1996: Diploma, Physics
(Freie Universität Berlin)
Thesis: Interactions of rigid membrane inclusions
1999: PhD, Physics
(Max Planck Institute of Colloids and Interfaces, Potsdam)
Thesis: Adhesion of multicomponent membranes
2000-2002: Postdoc
(University of California, San Francisco)
Since 2002: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

Proteins are chain molecules built from amino acids. The precise sequence of the twenty different types of amino acids in a protein chain defines into which structure a protein folds, and the three-dimensional structure in turn specifies the biological function of a protein. The reliable folding of proteins is a prerequisite for their robust function. Misfolding can lead to protein aggregates that cause severe diseases, such as Alzheimer's, Parkinson's, or the variant Creutzfeldt-Jakob disease.

To understand protein folding, researchers have long focused on metastable folding intermediates, which were thought to guide the unfolded protein chain into its folded structure. But about a decade ago, small proteins were discovered that fold without any detectable intermediates (see **Fig. 1**). This astonishingly direct folding from the unfolded state into the folded state has been termed 'two-state folding'. In the past years, the majority of small single-domain proteins have been identified as 'two-state folders'.

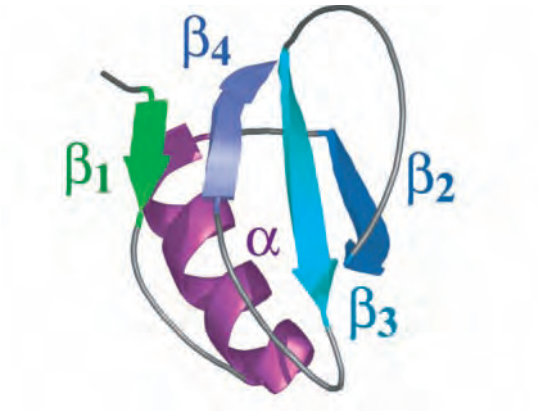


Fig. 1: The small protein CI2 is two-state folder, i.e. a protein that does not exhibit metastable intermediates states between the unfolded and the folded state. The structure of CI2 consists of an α-helix packed against a four-stranded β-sheet.

The characteristic event of two-state folding is the crossing of a barrier between the unfolded and the folded state (see **Fig. 2**). This folding barrier is thought to consist of a large number of extremely short-lived transition state structures. Each of these structures is partially folded and will either complete the folding process or will unfold again, with equal probability. In this respect, transition state structures are similar to a ball on a saddle point that has the same probability 1/2 of rolling to either side of the saddle (see **Fig. 3**).

Since transition state structures are highly instable, they cannot be observed directly. To explore two-state folding, experimentalists instead create mutants of a protein. The mutants typically differ from the original protein, the wild type, just in a single amino acid. The majority of these mutants still fold into the same structure. But the mutations may slightly change the transition state barrier and, thus, the folding time, the time an unfolded protein chain on average needs to cross the folding barrier (see **Fig. 4**).

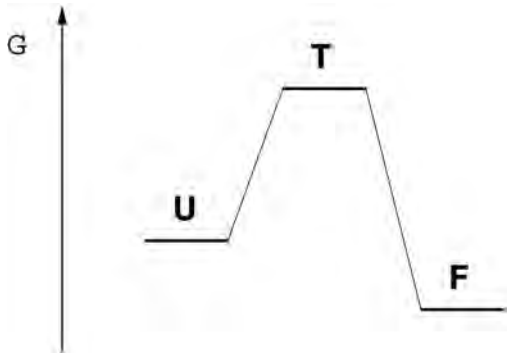


Fig. 2: The folding dynamics of two-state proteins is dominated by the transition state T between the unfolded state U and the folded state F. The transition state is a barrier in the free energy G. The folding time of a protein depends on the height of this free energy barrier.

The central question is how to reconstruct the transition state from the observed changes in the folding times. Such a reconstruction clearly requires experimental data on a large number of mutants. In the traditional interpretation, the structural information is extracted for each mutation independent of the other mutations. If a mutation does not change the folding time, then the mutated amino acid traditionally is interpreted to be still unstructured in the transition state. In contrast, if a mutation changes the folding time, the mutated amino acid is interpreted to be partially or fully structured in the transition state, depending on the magnitude of the change.

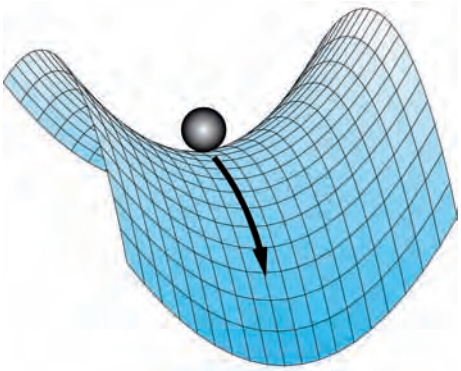


Fig. 3: A ball on a saddle point has the probability 1/2 of rolling to either side of the saddle. The transition state structures that make up the transition state correspond to such saddle points.

However, this traditional interpretation often is not consistent. For example, twenty single-residue mutations in the α-helix of the protein Chymotrypsin Inhibitor 2 (CI2) have very different effects on the folding time. Naively interpreted, these differences seem to indicate that some of the helical residues are unstructured in the transition state, while other residues, often direct neighbors, are highly structured. This

naive interpretation is in contradiction with the fact that the folding of helices is cooperative and can only occur if several consecutive helical turns are structured, stabilizing each other.

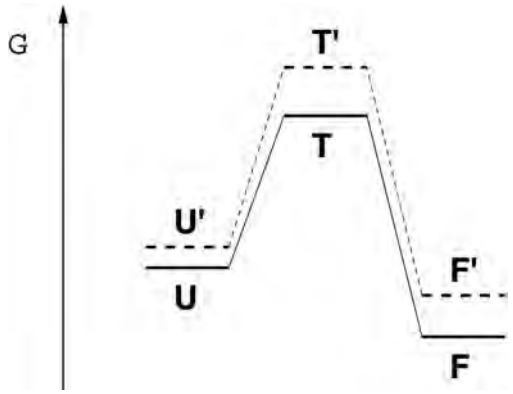


Fig. 4: Mutations of a protein shift the free energy of the unfolded state U, folded state F, and transition state T. The shift of the free energy barrier can be determined from experimentally measured folding times for the wildtype and the mutant proteins. Theoretical modelling of the experimental data leads to structural information on the transition state.

We have suggested a novel interpretation of the mutational data **[1,2]**. Instead of considering each mutation on its own, the new interpretation collectively considers all mutations within a cooperative substructure, such as a helix. In case of the α-helix of the protein CI2, this leads to a structurally consistent picture in which the helix is fully formed in the transition state, but has not yet formed significant interactions with the β-sheet. Also for other helices, we obtain a consistent structural interpretation of the mutational data **[2]**.

Currently, we focus on the construction of complete transition states from mutational data. An important step is to identify the cooperative subunits of a protein, which requires molecular modeling. To identify cooperative subunits of the protein CI2 (see **Fig. 1**), we have studied a large number of Molecular Dynamics unfolding trajectories **[3]**. On each unfolding trajectory, we determine the opening times of all amino-acid contacts of the folded structure. We find that the cooperative subunits of this protein correspond to four structural elements: the α-helix, and the three β-strand pairings $\beta_2\beta_3$, $\beta_3\beta_4$ and $\beta_1\beta_4$. We obtain high correlations between the opening times of contacts of the same structural elements, and observe lower correlations between contacts of different structural elements (see **Fig. 4**).

In addition, we have developed concepts that help to understand why some structural elements are central for the folding dynamics. The transition-state free-energy barrier of a protein is largely entropic. An important contribution is the loop-closure entropy that is lost when the protein chain forms contacts between amino acids during folding. This loss in loop-closure entropy depends on the sequence in which the contacts are formed **[4,5]**. Using graph-theoretical concepts to estimate loop lengths in a partially folded protein chain, we have identified contact sequences, or folding routes, with low entropy loss **[4]**. On these routes, some structural elements form early and effectively reduce the loop lengths of other structural elements, which results in a smaller entropy loss for forming the structural elements.

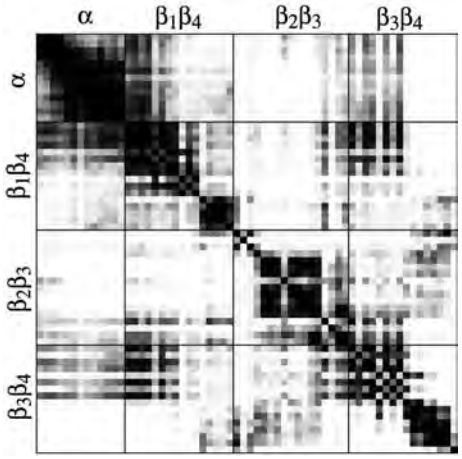


Fig. 5: Correlations between amino-acid contacts of the protein CI2 measured o a large number of Molecular Dynamics unfolding trajectories. The contacts are ordered according to the structural elements they belong to. Dark gray colors correspond to high correlations between pairs of contacts, light grey colors to low correlations. The dark colors along the diagonal of the correlation matrix indicate high correlations between contacts of the same structural element. The dark colors in the upper left square of the matrix, for example, indicate that the amino-acid contacts of the α-helix unfold highly cooperatively.

T. Weikl, C. Merlo, L. Reich
thomas.weikl@mpikg.mpg.de

References:

[1] Merlo, C., Dill, K.A., and Weikl, T.R.: Φ-values in protein folding kinetics have energetic and structural components. Proc. Natl. Acad. Sci. USA **102**, 10171-10175 (2005).

[2] Weikl, T.R., and Dill, K.A.: Transition states in protein folding kinetics: The structural interpretation of Φ-values. J. Mol. Biol. **365**, 1578-1586 (2007).

[3] Reich, L., and Weikl, T.R.: Substructural cooperativity and parallel versus sequential events during protein unfolding. Proteins **63**, 1052-1058 (2006).

[4] Weikl, T.R.: Loop-closure events during protein folding: Rationalizing the shape of Φ-value distributions. Proteins **60**, 701-711 (2005).

[5] Dixit, P.D., and Weikl, T.R.: A simple measure of native-state topology and chain connectivity predicts the folding rates of two-state proteins with and without crosslinks. Proteins **64**, 193-197 (2006).

Polymer Brushes

Christian Seidel 07.02.1949
1972: Diploma, Physics (Technical University Dresden) Thesis: Calculation of angular distribution and polarization of nucleon scattering close to resonance energies
1978: Dr. rer. nat., Polymer Physics (Institute for Polymer Chemistry, Teltow) Thesis: On the calculation of the phonon dispersion of solid polymers, application to polyvinylidenfluoride
1979-83: Research Scientist (Joffe Physico-Technical Institute, Leningrad)
1983-89: Research Scientist (Institute for Polymer Chemistry, Teltow)
1985: Dr. sc. nat., Solid State Theory (Institute for Polymer Chemistry, Teltow) Thesis: Ground states and critical temperatures in quasi-one-dimensional systems
1989-91: Group Leader (Institute for Polymer Chemistry, Teltow)
Since 1992: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
1994: Habilitation, Theoretical Chemistry (Technical University, Berlin)

Polymer brushes consist of chains densely end-grafted to a surface. Compared to polymers in solution, a new length scale is present in grafted systems: the distance between grafting points $d = A^{1/2}$ with A being the average area per polymer at the interface. When the grafting density $\rho_a = 1/A$ is high, nearby chains repel each other, forcing the polymer to stretch out away from the grafting plane. Such systems have important technological applications which range from colloidal stabilization and lubrication to nanoparticle formation at the polymer brush/air interface. In biological sciences, there is a growing interest in polymer brushes as model systems of cell surfaces.

If the grafted polymer is a polyelectrolyte (PEL), i.e., contains monomers which have the ability to dissociate charges in polar solvents such as, e.g. water, the behavior of the brush is basically governed by the osmotic pressure of free counterions. A strongly charged PEL brush is able to trap its own counterions generating a layer of high ionic strength. Therefore a surface coated with PELs is less sensitive to the salinity of the surrounding medium as a bare charged surface. Nevertheless varying salt concentration is an important parameter to tune the polyelectrolyte effect and to change the structure of PELs.

Polyelectrolyte Brushes with Additional Salt [1, 2]

According to Pincus **[3]** the PEL 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. The aim of our molecular dynamics (MD) simulation study was to clarify that question.

Fig.1a shows the brush height as a function of salt concentration where we plot $h(c_s)/h_{th}$ vs $bc_s/(\rho_a f^{1/2})$ with b being the monomer size and f the degree of dissociation. (In this study we use fully charged PELs, i.e., f = const = 1.) The brush height h_{th} is theoretically predicted to have the form $h_{th} = Nb\,(f + \sigma^2_{eff}\,\rho_a) / (1 + f)$ in the nonlinear osmotic regime without salt **[4]** with N being the chain length and σ_{eff} the effective polymer radius. Indeed all data points fall onto a universal scaling curve indicating again the validity of the nonlinear osmotic brush relation.

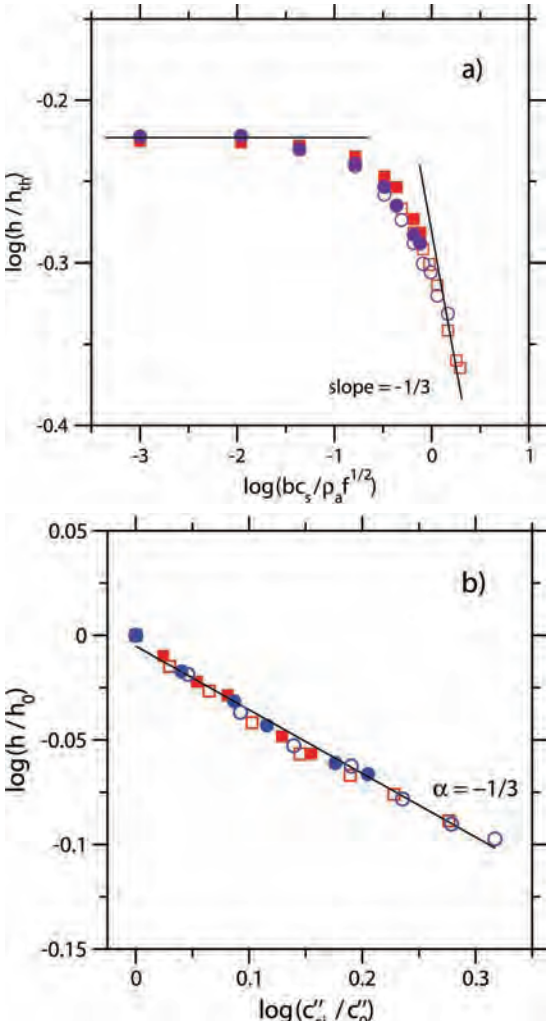


Fig. 1: Polyelectrolyte brushes with additional salt at grafting density 0.04 (circles) and 0.09 (squares). a) Brush height as a function of salt concentration, b) brush height as a function of total ion concentration.

For small c_s (i.e., $c_s << c_{ci}$ with c_{ci} being the counterion concentration), the influence of salt disappears. With growing c_s we obtain a broad cross over which merges at large salt concentration into the $c_s^{-1/3}$ power law predicted theoretically. However, the limit $c_s >> c_{ci}$ is hard to fulfill within the given numerical limitations. That is why we additionally study the brush height as a function of the total concentration of (free) ions inside the brush, i.e., taking into account counterions too. The corresponding plot is shown in **Fig. 1b** where we observe an almost perfect agreement with the scaling prediction.

Interacting Polyelectrolyte Brushes [2, 5]

PEL brushes attached to surfaces rubbing across an aqueous medium provide means of efficient lubrication. The interaction between two PEL brushes which are grafted to two apposing surfaces has recently received a lot of attention in experiments and simulations. Within the scaling approach **[3]** the disjoining pressure of two overlapping PEL brushes grafted to surfaces separated by a distance $2D$ is given by the counterion osmotic pressure $\Pi \sim k_B T f N \rho_a / D$. As the brushes are approaching two processes occur: interpenetration and compression.

Fig. 2 shows snapshots taken from simulations with varying distance between the two brushes. Note the strong exchange of counterions between the two brushes. At large separations the brush height remains almost constant. However, before overlapping at $D = h_{th}$ the chains begin to contract.

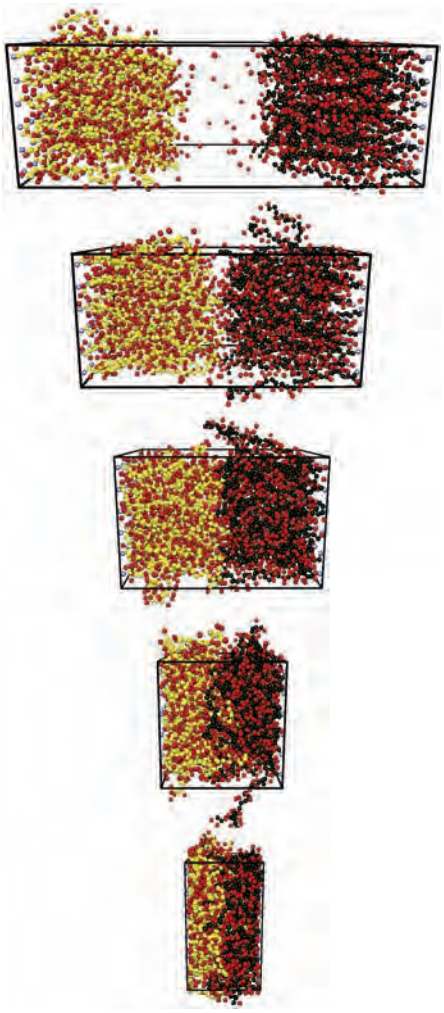


Fig. 2: Snapshots of two interacting polyelectrolyte brushes at decreasing separation D/h_{th} = 1.7, 1.2, 0.9, 0.6, and 0.3 from top to bottom. Monomers are colored yellow and dark green, respectively, counterions red.

In **Fig. 3** we plot the pressure as a function of separation. In fact, at $D > D^*$, the behavior of an ideal gas of counterions $\Pi \sim 1/D$ is reproduced. On the other hand, below D^* the pressure shows features expected in the excluded-volume-dominated regime. From our simulations, we find that the crossover occurs at $D^* \approx 1.4\ h_{th}$, i.e., before the two brushes strongly overlap. In the excluded-volume-dominated regime we observe a transition from good solvent behavior $\Pi \sim 1/D^2$ to θ behavior $\Pi \sim 1/D^3$ with increasing grafting density.

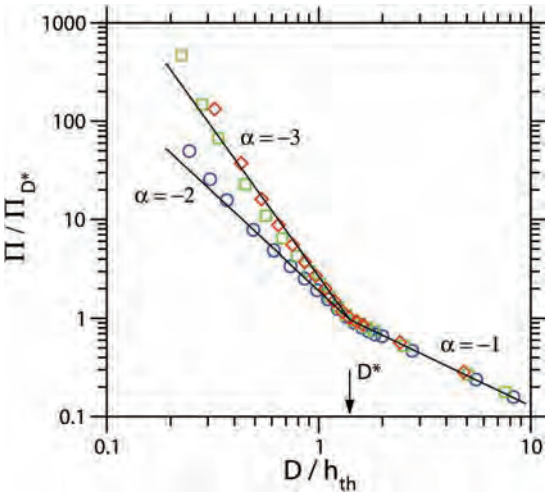


Fig. 3: Two interacting polyelectrolyte brushes. Pressure as a function of separation at grafting density 0.04 (circles), 0.09 (squares), 0.12 (diamonds).

DPD Simulation of Polymer Brushes [6]

The structure of (uncharged) polymer brushes was investigated by dissipative particle dynamics (DPD) simulations that include explicit solvent particles. With an appropriate choice of the DPD interaction parameters, we obtain good agreement with previous MD simulation results where the good solvent behavior has been modeled by an effective monomer-monomer potential. The relation between the Lennard-Jones length scale σ and the DPD scale r_c is found to be $r_c = 1.9\ \sigma$.

This study was implemented to benchmark DPD simulations of polymer brushes for subsequent large length scale simulations. DPD simulations to study nanoparticle aggregation inside a polymer brush are currently under progress.

C. Seidel, A. Kumar, S. Pal
seidel@mpikg.mpg.de

References:

[1] Kumar, N.A. and Seidel, C.: Polyelectrolyte Brushes with Added Salt. Macromol. **38**, 9341-9350 (2005).
[2] Kumar, N.A.: Molecular Dynamics Simulations of Polyelectrolyte Brushes. PhD Thesis, University of Potsdam (2006).
[3] Pincus, P.: Colloid Stabilization with Grafted Polyelectrolytes. Macromol. **24**, 2912-2919 (1991).
[4] Naji, A., Seidel, C. and Netz, R.R.: Theoretical Approaches to Neutral and Charged Polymer Brushes. Adv. Polym. Sci. **198**, 149-183 (2006).
[5] Kumar, N.A. and Seidel, C.: Interaction between Two Polyelectrolyte Brushes. Submitted to Phys. Rev. Lett.
[6] Pal, S. and Seidel, C.: DPD Simulations of Polymer Brushes. Macromol. Theory and Sim. **15**, 668-673 (2006).

Chemomechanical Coupling of Molecular Motors

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)

Living cells contain a large number of molecular motors: membrane pumps, stepping motors, growing filaments, and molecular assemblers such as polymerases and ribosomes. In many cases, these nanomachines are driven by the energy released from fuel molecules such as adenosine triphosphate (ATP). The coupling of the motor to these non-equilibrium reactions provides energy which is converted into conformational transformations of the motor and enables it to perform useful work.

Linear Stepping Motors with Two Motor Heads

The conversion of chemical energy into mechanical work is particularly striking for linear stepping motors such as kinesin, see **Fig. 1**, whose movements cover many length and time scales **[1]**. These motors have two heads, by which they bind to and walk along actin filaments and microtubules. In their bound states, they undergo cyclic sequences of conformational transitions, so-called motor cycles, that enable them to transform the chemical energy of single ATP molecules into discrete steps along the filament. Two-headed motors walk in a "hand-over-hand" fashion, i.e., by alternating steps in which one head moves forward while the other one remains bound to the filament.

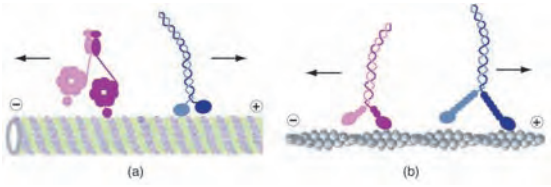


Fig. 1: Molecular motors that bind to and walk along cytoskeletal filaments, which are polar and have two different ends, a "plus" and a "minus" end: (a) Kinesin and dynein that move to the plus and minus end, respectively, of a microtubule; and (b) Myosin V and myosin VI that move to the plus (barbed) and minus (pointed) end, respectively, of an actin filament. The diameter of the microtubule and the actin filament are 25 nm and 8 nm, respectively. For simplicity, the cargo binding domains of the motors have been omitted. All four types of molecular motors are dimers consisting of two identical protein chains and use ATP hydrolysis in order to move in a directed manner. Kinesin and the two myosin motors walk in a "hand-over-hand" fashion.

Each step corresponds to a motor displacement of the order of 10 nanometers, comparable to the size of the motor heads. If there is no shortage of ATP, the motor kinesin, e.g., makes about 100 steps in one second which leads to a velocity of about one micrometer per second. The absolute value of this velocity is not very impressive, but relative to its size, the motor molecule moves very fast: On the macroscopic scale, its movement would correspond to an athlete who runs 200 meters in one second! This is even more surprising if one realizes that the motor moves in a very viscous and noisy environment since it steadily undergoes thermally excited collisions with a large number of water molecules.

Chemical States of Two-Headed Motors

In order to obtain a useful description of such a motor, we can first focus on the different chemical states of the two-headed motor. Each head has a catalytic domain, which is able to hydrolyze ATP into ADP plus P. The corresponding catalytic cycle consists of four subsequent transitions: binding of ATP, hydrolysis of ATP into ADP-P, release of P, and release of ADP. It is convenient to combine ATP hydrolysis and P release into a single transition and to distinguish 3 different states of a single motor head: state (T) with bound ATP, state (D) with bound ADP, or no bound molecule, i.e., empty (E), see **Fig. 2**. The two-headed motor can then attain 3 x 3 = 9 different chemical states and undergo transitions between these states as shown in **Fig.2**. In this figure, each motor state *i* corresponds to the vertex of a network graph. Every pair, *i* and *j*, of states is connected by two directed edges or di-edges corresponding to the forward transition I *ij* > from *i* to *j* and the backward transition I *ji* > from *j* to *i*. In **Fig. 2**, these two di-edges are combined into a single, undirected edge.

In general, the motor may undergo a chemical transition in which one of the catalytic motor domains changes its chemical composition or a mechanical transition corresponding to a mechanical step or substep. For the cytoskeletal motor kinesin, recent experiments indicate that this motor does not exhibit mechanical substeps on the timescale of microseconds **[2]**. In **Fig. 2**, chemical and mechanical transitions are indicated by solid and broken lines, respectively.

The chemical kinetics of the two heads is coordinated: binding of ATP to one head leads to the release of ADP from the other head. The tight coupling of ATP hydrolysis and stepping as well as the hand-over-hand movement indicate that such an out-of-phase behavior of the two heads also governs the catalytic action of stepping kinesin. In order to describe this behavior, we may omit all states in **Fig. 2(a)** for which both heads have the same chemical composition. In this way, we arrive at the reduced state space shown in **Fig. 2(b)** which consists of only six states.

Nonequilibrium Processes and Motor Cycles

Nonequilibrium processes are intimately related to cycles in state space and nonzero fluxes along these cycles. Each cycle, C, consists of two directed cycles or dicycles, C+ and C-, that differ in their orientiation. The network graph in Fig. 2(a) contains a huge number of cycles (more than 200) whereas the one in **Fig. 2(b)** contains only three cycles. Two of these latter cycles, namely <25612> and <52345>, contain both a hydrolysis transition, during which the motor consumes chemical energy, and a mechanical stepping transition, during which the motor can perform mechanical work.

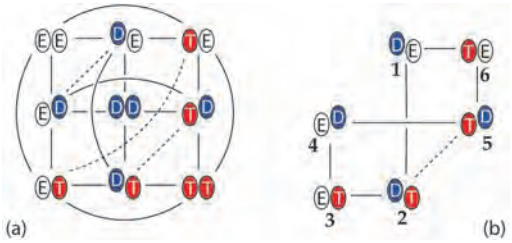


Fig. 2: Network graph with 9 states for a molecular motor with two catalytic domains, each of which can be empty (E), or bind an ATP (T) or ADP (D) molecule. This network contains 21 edges representing 18 chemical forward and backward transitions (solid lines) as well as 3 mechanical forward and backward steps (broken lines); and (b) Reduced state space with 6 states obtained from the 9-state network in (a) by omitting the three states E-E, T-T, and D-D. This network contains 7 edges corresponding to 6 chemical transitions (full lines) plus 1 mechanical transition (broken line).

Steady State Balance Conditions

In our theory, the dynamics of the motor is described by a continuous-time Markov process with transition rates ω_{ij} from state *i* to state *j*. Each dicycle can be characterized, in the steady state of the motor, by a statistical entropy that is produced during the completion of this dicycle **[3]**. Identifying this statistical entropy with the heat released by the motor and using the first law of thermodynamics, we have derived rather general steady state balance conditions of the form

$$k_B T \sum_{ij} \ln(\omega_{ij} / \omega_{ji}) = E_{ch}(C+) - W_{me}(C+)$$

that relate the transition rates ω_{ij} to the chemical energy, $E_{ch}(C+)$, consumed and the mechanical work, $W_{me}(C+)$, performed during the cycle C+. The basic energy scale is provided by the thermal energy $k_B T$, the summation runs over all di-edges I *ij* > of the dicycle C+.

The mechanical work is determined by external load forces experienced by the motor and vanishes in the absence of such forces. This implies that one can decompose the steady state balance conditions into a zero-force and a force-dependent part. In addition, it is straightforward to include other energetic processes into the steady state balance conditions. Two examples are (i) energy input arising from the adsorption of photons and (ii) work against an electrochemical potential. **[3]**

Kinesin's Network of Motor Cycles

In principle, both the transition rates ω_{ij} and the energetic terms on the right hand side of the steady state balance conditions can be measured. If such a complete set of experiments were available for a certain motor, one could use the balance conditions to estimate the experimental accuracy. In practise, some of the transition rates will be difficult to measure, and the balance conditions can then be used to estimate the values of the unknown rates.

We have recently applied this latter strategy to the cytoskeletal motor kinesin **[4]**. One important consequence of our analysis is that the stall force of the motor is determined by the flux balance of two different cycles that govern the forward and backward mechanical step and both involve the hydrolysis of one ATP molecule. This differs from previous unicycle models in which the stall force was determined by the flux balance between the two dicycles of the same cycle. The latter flux balance is, however, not possible for small ADP concentrations as typically considered in motility assays. A detailed comparison between our theory and the experimental data of Ref. **[2]** is shown in **Fig. 3**. In fact, our theory provides a quantitative description for all motor properties as observed in single molecule experiments **[4]**.

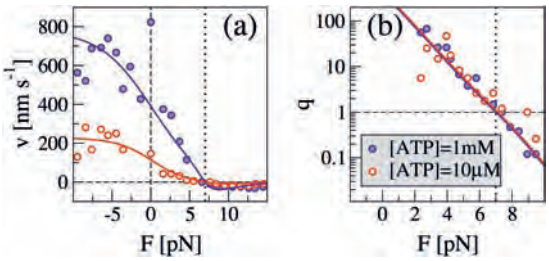


Fig. 3: (a) The motor velocity v and (b) the ratio q of the number of forward to the number of backward mechanical steps as a function of external load force F. The data are for drosophila kinesin and taken from Ref. [2]. The solid lines are calculated using the 6-state network in Fig.2(b). The vertical dotted line corresponds to the stall force at which the velocity vanishes.

R. Lipowsky, S. Liepelt
reinhard.lipowsky@mpikg.mpg.de

References:

[1] Lipowsky, R., Chai, Y., Klumpp, S., Liepelt, S., and Müller, M.J.I., Molecular Motor Traffic: From Biological Nanomachines to Macroscopic Transport, Physica A **372**, 34 (2006).

[2] Carter, N.J. and Cross, R.A.: Mechanics of the kinesin step, Nature **435**, 308 (2005).

[3] Liepelt, S., and Lipowsky, R.: Steady state balance conditions for molecular motor cycles and stochastic nonequilibrium processes, EPL **77**, 50002 (2007).

[4] Liepelt, S., and Lipowsky, R.: Kinesin's network of chemomechanical motor cycles, Phys. Rev. lett. (in press, 2007).

Cooperative Transport by Molecular Motors

Stefan Klumpp 29.09.1973
1999: Diploma, Physics
(University of Heidelberg)
Thesis: Noise-Induced Transport
of Two Coupled Particles
2003: PhD, Physics
(Max Planck Institute of Colloids
and Interfaces, Potsdam)
Thesis: Movements of Molecular
Motors: Diffusion and Directed Walks
Since 2004: Group Leader
(Max Planck Institute of Colloids
and Interfaces, Potsdam)
Since 2006: Postdoc
(University of California, San Diego)

Molecular motors are proteins that transform chemical energy into work and directed movement. Our group is particularly interested in cytoskeletal motors which transport cargoes along the tracks provided by the filaments of the cytoskeleton. Our current understanding of these motors is to a large extent based on biomimetic model systems which consist of only a small number of different components such as motors, filaments, and ATP, the chemical fuel used by these motors. These systems allow us to study molecular motors systematically within a controlled environment.

Important quantities that characterize molecular motors are their velocity and their run length. The latter quantity describes the distance over which the motor moves along the filament before it falls off the track. This run length is typically 1 µm for a single motor molecule. Such unbinding events are unavoidable for molecular motors since they constantly undergo thermal collisions with other molecules.

Cooperative Cargo Transport by Several Motors

In cells, cargo particles such as vesicles and organelles are usually transported by teams of several molecular motors. Because each motor unbinds from and rebinds to the filament, the actual number of motors is not fixed but varies with time. We have developed a model for this type of transport process based on the known properties of single motor molecules **[1]**. This model describes the movement of a cargo particle to which a number N of motors are immobilized. These motors bind to and unbind from a filament in a stochastic manner, so that the number of motors that actually pull the cargo changes stochastically between 1 and N, as shown in **Fig. 1**. The theoretical predictions derived from our model are accessible to in vitro experiments using the same techniques that have been used to study single motors.

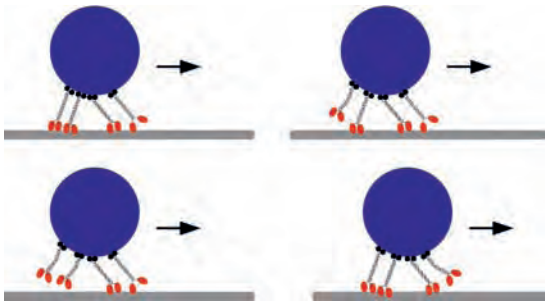


Fig. 1: A cargo particles (blue) is pulled along a filament (grey rod) by four molecular motors. These motors bind to the filament and unbind from it in a stochastic manner, so that the number of actually pulling motors changes between 1 and 4.

The main effect of motor cooperation is an enormous increase in run length, which depends exponentially on the number of motors. We have estimated that 7-8 motors are sufficient for transport over centimetres and that the cooperation of 10 motors leads to run lengths of over a meter **[1]**. Transport over such long distances occurs in the axons of nerve cells, which represents the biggest challenge for long-range transport in cells. The increase in run length has recently been confirmed in experiments done in the group of R. Dimova using latex beads pulled by varying numbers of kinesin motors.

If the cargo is pulled against an opposing force, its movement is slowed down. In addition, the force increases the motors' tendency to unbind from the filament. Since unbinding of motors increases the force that the remaining bound motors have to sustain, this increases their unbinding probability even further and leads to a cascade of unbinding events. As a result of these unbinding cascades, the force-velocity relationship for a cargo pulled by several motors is markedly non-linear, in contrast to the approximately linear force-velocity relations observed for single motors (see **Fig. 2**).

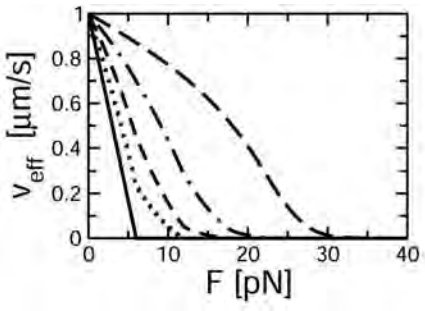


Fig. 2: The force-velocity relation for cargoes transported cooperatively by N motors against an opposing force F. The graph shows curves for N=1,2,3,5, and 10 (from left to right). While the velocity exhibits a linear decrease for a single motor, the curves are non-linear for transport by more than one motor due to the forced decrease of the number of bound motors.

Unbinding cascades also play an important role in systems where cargoes are pulled by two types of motors which move into opposite directions. In that case, the unbinding cascades lead to a tug-of-war-like instability. As a consequence of that instability, the cargo is not stalled by being pulled into opposite directions, but rather switches stochastically between quick runs back and forth **[2]**.

Active Diffusion

Passive diffusion or Brownian motion is too slow to transport larger objects such as vesicles and organelles within cells. This fact is usually taken as an argument for the necessity of active transport. Active transport, however, is not necessarily directed, but can also be used to generate effectively diffusive movements, e.g. if the direction of motion of a motor-driven cargo particles changes from time to time in a random fashion. We call the resulting diffusive, but energy-consuming movements *active diffusion*. There are examples for active diffusion within cells, but active diffusion can also be used in artificial systems as a method to speed up diffusive processes such as the search for an immobile binding partner. Such artificial systems can be expected to have many applications in bionanotechnology. We have studied active diffusion for several systems with regular arrangements of filaments on structured surfaces (see **Fig. 3**) which can be prepared using a number of techniques established during recent years. Our theoretical results indicate that active diffusion is most useful for the transport of large objects – for micron-sized particles in water active diffusion can be 100 times faster than passive Brownian motion – and/or for transport in very viscous environments. Again the cooperation of several motors is helpful, since the maximal active diffusion coefficient that can be generated is proportional to the product of run length and motor velocity.

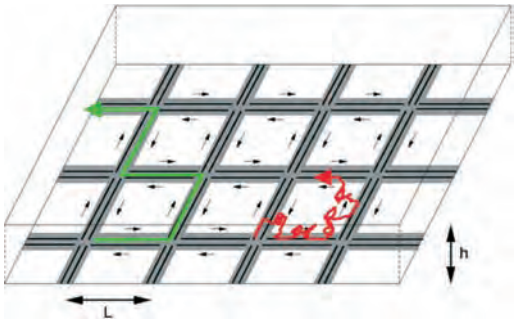


Fig. 3: An array of filaments (black lines) specifically adsorbed on a structured surface. The molecular motor-driven movements along such filament systems exhibit active diffusion, energy-consuming, but effectively diffusive movements as indicated by the green and red trajectories. The characteristic diffusion coefficient of these movements can be much larger than the usual diffusion coefficient which arises from Brownian motion.

Traffic Phenomena

If many molecular motors (or cargo particles pulled by molecular motors) move along the same filament, the traffic may become congested. In contrast to the familiar vehicular traffic jams, however, molecular motors can escape from a congested filament by unbinding from it. We have studied traffic jams of molecular motors that arise from different types of bottlenecks and in different types of compartments **[4]**. In particular, we have recently studied the effect of defects on the filaments and the influence of the compartment geometry on the length of traffic jams. In the latter project, we found that in several types of tube-like compartments, traffic jams are strongly enhanced by the compartment geometry.

S. Klumpp, Y. Chai, M. Müller, R. Lipowsky
klumpp@mpikg.mpg.de

References:

[1] Klumpp, S. and Lipowsky, R.: Cooperative cargo transport by several molecular motors. Proc. Natl. Acad. Sci. USA **102**, 17284-17289 (2005).
[2] Müller, M. J. I., Klumpp, S. and Lipowsky, R.: (to be published)
[3] Klumpp, S. and Lipowsky, R.: Active diffusion by motor particles. Phys. Rev. Lett. **95**, 268102 (2005).
[4] Klumpp, S., Müller, M. J. I. and Lipowsky, R.: Traffic of molecular motors. In: Traffic and Granular Flow '05, edited by Schadschneider, A. et al. (Springer, Berlin 2007), pp.251-261.

Polymerization of Filaments

Julian Charles Shillcock 18.10.1960
1982: B.Sc (Hons), Physics (Kings College London)
1985: M.Sc, Nuclear Physics (Simon Fraser University, Canada)
Thesis: Hanbury-Brown Twiss Effect in Heavy-Ion Collisions
1986-1990: Research Scientist (British Aerospace, Space Systems Division, U.K.)
1995: PhD, Biophysics (Simon Fraser University, Canada)
Thesis: Elastic Properties of Fluid and Polymerised Membranes under Stress
1995-1997: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
1998-1999: Senior Scientist (Molecular Simulations Inc., Cambridge, U.K.)
1999-2003: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
2004-2007: External Research Associate (Max Planck Institute of Colloids and Interfaces, Potsdam)

The cytoskeleton of a cell is a major structural component that gives rigidity and support to the plasma membrane and participates in numerous cellular processes. It is composed of rodlike filaments of varying degrees of rigidity that self-assemble, and disassemble, in response to cellular signals. Actin filaments form one part of the cytoskeleton, and are composed of many hundreds of actin monomers that bind together into linear and branched filaments. Each monomer is a globular protein approximately 5 nm in diameter that contains a bound ATP molecule whose hydrolysis, and subsequent phosphorylation, provides the energy required to drive filament growth. In motile cells, actin filaments continually form and disassemble in a process that requires the consumption of ATP. This process is referred to as treadmilling, and is the basis for cell crawling. Although experiments have revealed many fascinating aspects of actin treadmilling in generating cellular motion, the molecular details of the process are still unclear. Molecular Dynamics simulations of small sections of filaments have shown the importance of electrostatic interactions in guiding the monomers onto the ends of the filament, and the kinetics of monomer addition and loss at the two ends of a short filament **[1]**. However, these highly-detailed simulations are limited to short lengths of filament because of their computational cost.

In order to visualize F-actin growth and treadmilling in filaments containing hundreds or thousands of monomers, we are using Brownian Dynamics simulations without an explicit solvent. Each actin monomer moves under the influence of forces between monomers, but has a bulk diffusion coefficient that is a parameter of the simulation. The absence of solvent particles allows simulations of filament growth over times approaching several milliseconds. Actin monomers are represented as polar rigid bodies that diffuse freely around the simulation box and, if they encounter the ends of a filament, can bind to it. The terminal monomers can also unbind from a filament at a constant rate (**Fig. 1**).

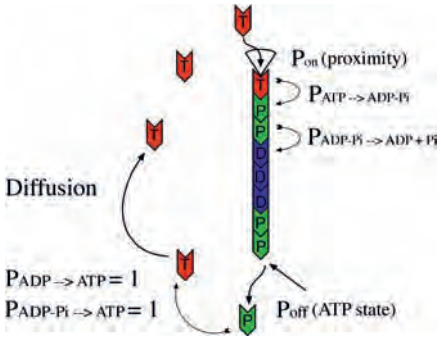


Fig. 1: Diagram showing how the attachment and detachment of actin monomers from a filament is modelled in the simulations. Monomers diffusing in the bulk possess a bound ATP molecule (red monomers). Once a monomer binds to a filament, its ATP molecule has a certain probability of being hydrolysed to ADP with a bound Pi (green monomers). Later, the bound Pi can dissociate leaving the monomer with a bound ADP. The probability for the two terminal monomers of a filament to detach may depend on the monomer's internal state. The ATP molecules are not explicitly modelled in the simulations, but each actin monomer has an internal flag that represents its ATP state. Monomers may be restricted to a single state by setting the probability of ATP hydrolysis to zero, or may be given two states if the probability of the transition from ADP with bound Pi to ADP is set to zero. In the most general case, the internal flag has three states with three transition probabilities. All monomers that detach from a filament are instantaneously converted to ATP monomers as the phosphorylation of the freely-diffusing actin monomers is expected to occur more rapidly than the attachment of monomers to a growing filament in the experiments of interest.

The two ends of F-actin filaments are referred to as the barbed and pointed ends, and are not equivalent. The rates of monomer attachment and detachment are typically different for the two ends, attachment being faster at the barbed end while detachment occurs faster at the pointed end. Monomers have an internal flag that represents the state of a bound ATP molecule: it takes the values ATP, ADP with bound inorganic phosphate, ADP-Pi, and ADP with the phosphate released. The unbinding rates at the filament's ends depend on the terminal monomer's internal state.

Kunkun Guo, a post-doctoral fellow, has been exploring various quantitative measures of a filament's properties and growth behaviour. The stiffness of a single filament is measured from its shape fluctuations in an external potential, and the attachment and loss of actin monomers to a filament is studied as a simple model of treadmilling. Our preliminary results on filament growth are in agreement with previous theoretical models **[2]** in which multiple states of bound ATP/ADP in the actin monomers are required in order to reproduce the observed properties of actin filaments, including the fluctuations in length of a filament as a function of bulk monomer concentration. It currently appears that a filament composed of actin monomers with only one internal ATP state grows tran-

siently but then disintegrates. Monomers that have two internal states appear to show transient periods of treadmilling. A snapshot of a growing filament that consists of monomers with three internal states is shown in **Fig. 2**.

Fig. 2: Snapshot of a growing filament composed of monomers with 3 internal states. The bulk of interior of the filament is made up of monomers with bound ADP (shown in blue) whereas the two ends are composed of monomers with bound ATP (red) or ADP-Pi (green). The sizes of the caps are different at the two ends because the probability of the terminal monomer detaching depends on the state of the monmer, and the precise values are chosen to be different for the two ends.

The bulk of the filament consists of ADP monomers (shown in blue), while the two ends consist of short caps of ADP-Pi (green monomers) and ATP monomers (red). The lengths of the caps, and their proportions of red to green monomers, are different because the detachment probabilities of the monomers depend on the monomer internal state and are chosen to be different at each end to reflect the polar character of actin monomers in the experiments. We are exploring the model's parameter space to see if treadmilling can be observed as a steady-state phenomenon, and to measure quantitative properties of the process **[3]**. **Fig. 3** shows preliminary results for the fluctuating length of a filament composed of monomers with only a single internal state.

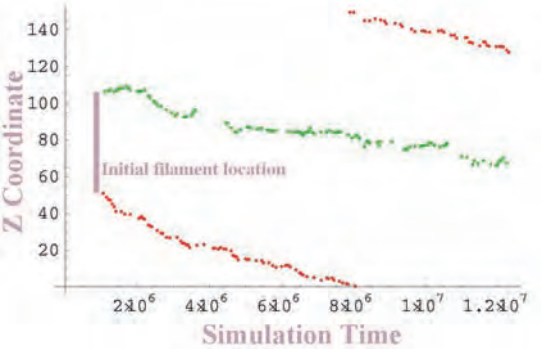


Fig. 3: Plot of the z coordinates of the newly-attached terminal monomers of a growing filament as a function of time. When a monomer attaches to the filament its instantaneous z coordinate is recorded. The two ends of the filament are shown in different colours with the pointed end in green and the barbed end in red, but these do not correspond to the orientation of the barbed and pointed ends shown in Fig. 1. We allow the filament to grow to a certain length before we start measuring its properties. An increasing gap between the two curves indicates that the filament is increasing in length, whereas a decreasing gap shows that it is shrinking. The discontinuity in the red curve at approximately 8,000,000 timesteps is due to the filament extending across the periodic boundary at the z ends of the simulation box.

The filament appears to increase in length continuously throughout the simulation period (the red and green curves move apart). This indicates that this particular filament is not treadmilling. **Fig. 4** shows the distribution of the time intervals between monomer-binding events for the two ends of the same filament as **Fig. 3**. The distribution is approximately exponential, although the relatively small number of data points (65) does not allow a definitive conclusion. This work is continuing.

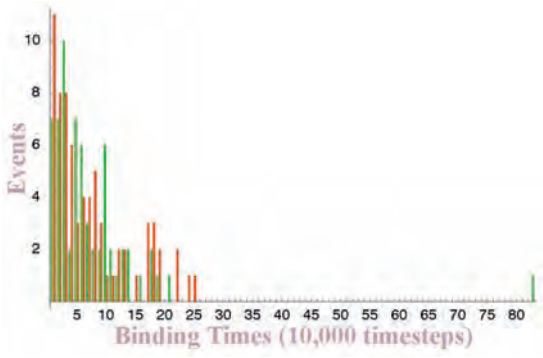


Fig. 4: Histogram of the distribution of time intervals between successive monomers attaching to the two ends of a growing filament (green curve is the filament's pointed end, the red curve is its barbed end). The width of the bins is 10,000 timesteps, and the probability of attachment is seen to be approximately exponentially distributed.

J. C. Shillcock, K. Guo, R. Lipowsky.
Julian.Shillcock@mpikg.mpg.de

References:

[1] Sept, D. and McCammon, J. A., Thermodynamics and kinetics of actin filament nucleation. Biophys. J. **81**, 667-674 (2001).

[2] Vavylonis, D., Yang, Q. and O'Shaughnessy, B. Actin polymerization kinetics, cap structure and fluctuations. PNAS. **102**, 8543-548 (2005).

[3] Guo, K., Shillcock, J. C. and Lipowsky, R. Self-assembly, growth and treadmilling of actin filaments in coarse-grained simulations. JACS. (to be published 2007).

Semiflexible Polymers and Filaments

Jan Kierfeld 31.01.1969
1993: Diploma, Physics
(University of Cologne)
Thesis: On the Existence of the Vortex Glass Phase in Layered Systems
1995-1996: Research Associate
(UC San Diego, California)
1996: PhD, Physics
(University of Cologne)
Thesis: Topological Order and Glassy Properties of Flux Line Lattices in Disordered Superconductors
1997-2000: Postdoc
(Argonne National Laboratory, Illinois)
Since 2000: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)
2006: Habilitation
(University of Potsdam)
Thesis: Strings and Filaments: From Vortices to Biopolymers

Many biopolymers such as DNA, filamentous (F-) actin or microtubules belong to the class of semiflexible polymers. The biological function of these polymers requires considerable mechanical rigidity. For example, actin filaments are the main structural elements of the cytoskeleton in which actin filaments form 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 stimuli. Synthetic semiflexible polymers also play an important role in chemical physics. Prominent examples are polyelectrolytes or dendronized polymers, where the electrostatic repulsion of charges along the backbone or the steric interaction of side groups gives rise to considerable bending rigidity.

The bending rigidity of semiflexible polymers is characterized by their persistence length **[1]**, which is given essentially by the ratio of bending rigidity κ and thermal energy. The physics of semiflexible polymers becomes qualitatively different from the physics of flexible synthetic polymers on length scales smaller than the persistence length where bending energy dominates over conformational entropy. Typical biopolymer persistence lengths range from 50nm for DNA to the 10m-range for F-actin or even up to the mm-range for microtubules and are thus comparable to typical contour lengths such that semiflexible behaviour plays an important role.

We theoretically investigate the physics of semiflexible polymers and filaments from the single polymer level to biological structures consisting of assemblies of interacting filaments. This requires exploring the interplay of thermal fluctuations, external forces, interactions, and active fluctuations in filament systems.

Single Filaments:
Fluctuations, Confinement, and Manipulation

The persistence length of a semiflexible polymer gives a typical length scale for its thermal shape fluctuations. The bending energy couples shape fluctuations of different wavelengths. Using a functional renormalization group approach, we calculated how this results in a softening of the polymer with an exponential decay of its bending rigidity for large wavelength fluctuations. This effect provides a concise definition of the persistence length as the characteristic decay length of the bending rigidity **[1]**.

Thermal fluctuations of confined filaments are not only characterized by their persistence length but also by the so-called deflection length, which is related to the confining geometry. In a recent study **[2]** we performed a quantitative fluctuation analysis for actin filaments confined to microchannels and determined both persistence and deflection length.

During the last decade, micromanipulation techniques such as optical tweezers and atomic force microscopy (AFM) have become available which allow the controlled manipulation of single polymers and filaments. Experiments such as pulling single 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 such experiments quantitatively, theoretical models are necessary, which we developed for (i) force-induced desorption or unzipping of filaments **[3]** and (ii) the activated dynamics of semiflexible polymers on structured substrates **[4,5]**.

AFM tips or optical tweezers can be used to lift an adsorbed semiflexible polymer from a surface or unzip two bound semiflexible polymers (**Fig.1**). We can calculate the resulting force-extension characteristics for such a force-induced desorption process **[3]**. One interesting feature is the occurrence of an energetic barrier against force-induced desorption or unzipping which is solely due to the effects from bending rigidity (**Fig.1**).

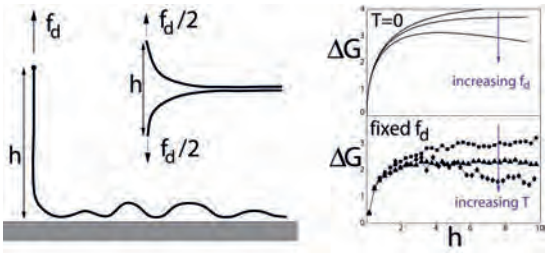


Fig. 1: Left: Force-induced desorption of an adsorbed filament and unzipping of two bound filaments. Right: Free energy landscapes for force-induced desorption as a function of the height h of the polymer end. The polymer desorbs either upon increasing the desorbing force f_d or the temperature T. Both processes are governed by a free energy barrier.

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 point forces 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]**.

Structured adsorbed surfaces can also give rise to confinement effects that result in morphological shape transitions of single semiflexible polymers. Currently, we are investigating the morphological diagram for semiflexible polymer rings on a structured substrate containing an adhesive stripe (**Fig.2**). Upon increasing the adhesive potential of the stripe the polymer undergoes a morphological transition from an elongated to a round conformation.

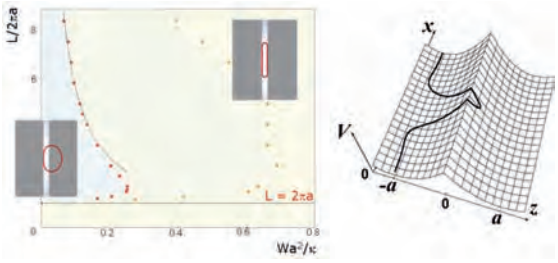


Fig. 2: Right: Kinked conformation of a semiflexible polymer, which is pushed at its mid-point over a potential barrier. Left: Morphological diagram of a semiflexible polymer ring adsorbed on a substrate containing an adhesive stripe of width a as a function of the polymer length L and the ratio of adhesive strength of the stripe and the polymer bending rigidity. In the red region at high adhesive strength, the ring assumes an elongated conformation within the stripe; in the blue region it exhibits a round conformation dominated by bending energy.

Filament Assemblies

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, 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**).

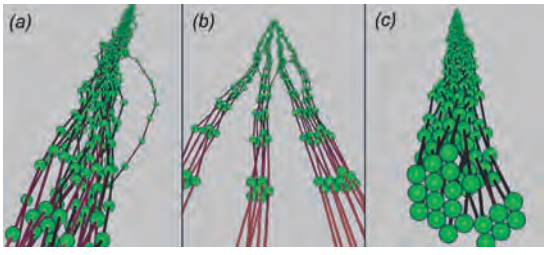


Fig. 3: Three snapshots of a bundle formed by twenty filaments as observed in computer simulations: (a) Loose bundle for a crosslinker concentration that is only slightly above the threshold value; (b) and (c) show two different conformations of the same bundle corresponding to a segregated conformation with three sub-bundles and a compact conformation with roughly cylindrical shape, respectively.

Active Filament Systems

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). For filament bundles, this active polymerisation dynamics can be used for force generation. We found that filament bundles can generate polymerization forces but also zipping forces by converting the gain in adhesive energy upon bundling into a force exerted on a confining wall **[7]**.

Cytoskeletal filaments 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 motor proteins are immobilized onto a glass plate and actively pull filaments over this surface. Computer simulations and theoretical arguments show that the active driving by molecular motors enhances the tendency of filaments to align: As one increases the density of molecular motors, the system undergoes a phase transition into a nematic liquid crystal (**Fig.4**) **[8,9]**. This ordering effect arises from the interplay of the active driving by molecular motors and steric interactions between filaments. We were able to describe the resulting phase diagram of this non-equilibrium filament system quantitatively in terms of experimentally accessible model parameters by introducing the concept of an effective increased filament length **[8]**. The density of inactive motors and microscopic motor parameters such as detachment and stall forces determine the formation of a new non-equilibrium phase, a kinetically arrested cluster phase with mutually blocking filaments **[9]**.

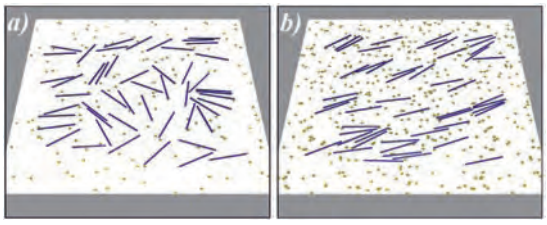


Fig. 4: Two snapshots of rodlike filaments (blue) on a surface coated with immobilized molecular motors (yellow). (a) At low motor surface density the filaments display no order. (b) Above a threshold value for the motor density, the filaments spontaneously order into a parallel pattern. This "active nematic ordering" is caused by the interplay of filament collisions and their motor-driven motion.

J. Kierfeld, K. Baczynski, K. Goldammer, P. Gutjahr, T. Kühne, P. Kraikivski
Jan.Kierfeld@mpikg.mpg.de

References:

[1] Gutjahr, P., Lipowsky, R., Kierfeld J.: Persistence length of semiflexible polymers and bending rigidity renormalization. Europhys. Lett. **76**, 994-1000 (2006).
[2] Köster, S., Stark, H., Pfohl, T., Kierfeld, J.: Fluctuations of Single Confined Actin Filaments, Biophys. Rev. Lett., in press (2007).
[3] Kierfeld, J.: Force-Induced Desorption and Unzipping of Semiflexible Polymers, Phys. Rev. Lett. **97**, 058302 (2006).
[4] Kraikivski, P., Lipowsky, R., Kierfeld, J.: Activated dynamics of semiflexible polymers on structured substrates, Eur. Phys. J. E **16**, 319-340 (2005).
[5] Kraikivski, P., Lipowsky, R., Kierfeld, J.: Point force manipulation and activated dynamics of semiflexible polymers on structured substrates, Europhys. Lett. **71**, 138-144 (2005).
[6] Kierfeld, J., Kühne, T., Lipowsky, R.: Discontinuous unbinding Transitions of Filament Bundles, Phys. Rev. Lett. **95**, 038102 (2005).
[7] Kierfeld, J., Gutjahr, P., Kühne, T., Kraikivski, P., Lipowsky, R.: Buckling, Bundling, and Pattern Formation: From Semi-Flexible Polymers to Assemblies of Interacting Filaments, J. Comput. Theor. Nanosci. 3, 898-911 (2006).
[8] Kraikivski, P., Lipowsky, R., Kierfeld, J.: Enhanced Ordering of Interacting Filaments by Molecular Motors, Phys. Rev. Lett. **96**, 258103 (2006).
[9] Kierfeld, J., Kraikivski, P., Lipowsky, R.: Filament Ordering and Clustering by Molecular Motors in Motility Assays, Biophys. Rev. Lett. 1, 363-374 (2006).

Fractionation and Low-Density-Structures in Systems of Colloidal Rods

Thomas Gruhn 10.06.1969
1995: Diploma, Physics (Technische Universität Berlin)
Thesis: Monte-Carlo-Untersuchungen der Ausrichtung nematischer Flüssigkristalle (A Monte Carlo study of the alignment in nematic liquid crystals)
1998: PhD, Physics (Institut für Theoretische Physik, TU Berlin)
Thesis: Substrate-induced order in confined molecularly thin liquid-crystalline films
1999: R&D Project (Siemens AG, Berlin)
2000: Postdoc (University of Massachusetts, USA)
2001: Group Leader (Max Planck Institute for Colloids and Interfaces, Potsdam)

Rigid rods of mesoscopic size can nowadays be synthesized in large amounts. Examples are carbon nanotubes, boehmite needles, cylindrical dendrimers, and metallo-supramolecular polyelectrolytes (see references in **[1]**). Colloidal rods are of great relevance for the creation of mesoscopic structures. In solution they can self-organize and induce long-range spatial and orientational order. Typical examples are liquid-crystalline mesophases, known from systems of small liquid crystal molecules. There are, however, important differences between traditional liquid crystals and systems of mesoscopic rods. While systems of small liquid crystal molecules are typically monodisperse or consist of a small number of components, most systems of synthesized colloidal rods have a polydisperse length distribution, due to the production method. Furthermore, the alignment of small rods is mainly caused by a coupling of the molecules' polarization axes, while orientational order of mesoscopic rods is typically based on steric interactions. Therefore, in many cases colloidal rods can be successfully approximated as hard spherocylinders. However, if van-der-Waals forces between the colloidal rods cannot be neglected or if the solvent generates strong depletion forces between adjacent rods, attractive interactions must be considered.

Fractionation in Systems of Chemically Homogenous Rods

Polydisperse systems of spherocylindrical rods have a pressure range in which an isotropic phase with no orientational order coexists with a phase which is (at least) orientationally ordered. In this case, long rods are preferentially found in the ordered phase while the majority of small rods is located in the isotropic phase. With the help of Monte Carlo simulations we have investigated the influence of attractive interactions on fractionation effects in a polydisperse system of spherocylinders **[2]**. A spherocylinder consists of a cylinder of diameter D and length $L=\lambda D$, which is capped by two hemispheres with diameter D. We analyzed a polydisperse system of rods with cylinder lengths between $\lambda=1$ and $\lambda=8$ for various reduced pressures $P^*=Pv_{av}/T$, where v_{av} is the average rod volume and T is the thermal energy including the Boltzmann factor k_B. At large pressures long rods are strongly aligned while the orientational order for short rods is low. The discrepancy between the order of short and long rods is strongly enhanced by attractive interactions (**Fig. 1**).

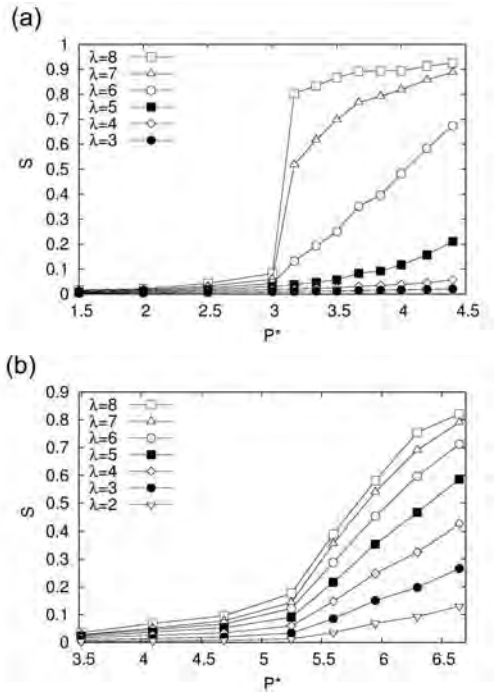


Fig. 1: Orientational order parameter S of components with cylinder length λ in a polydisperse rod system at reduced pressure P. (a) In a system of attractive rods, long rods are strongly aligned at pressures P*>3, while short rods are almost isotropic.(b) For hard rods), the orientational order decreases gradually with the rod length.*

An analysis of the local structure reveals that, at high pressures, long attractive rods form a smectic monolayer with hexatic in-plane order, while hard rods form a less ordered nematic droplet which consists of preferentially long rods (cmp. **Fig. 2**).
This corresponds to experimental results for fd-viruses in a polymer solution which form strongly ordered mono-layers in the presence of strong depletion forces and less ordered domains if depletion forces are weak **[3]**.

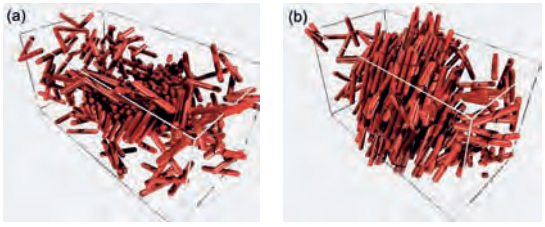


Fig. 2: Typical configurations for polydisperse systems of (a) attractive and (b) hard rods. For clarity reasons short rods (λ<5) are omitted. In (a) long rods aggregate to a smectic monolayer, in (b) a nematic droplet forms.

Spatial fractionation can also be induced by an adjacent, structured substrate. For this purpose, substrates with rectangular cavities turned out to be particularly suited. **Fig. 3** shows configurations of an equilibrated rod system with four different lengths in contact with a substrate with cavities of different sizes. Starting from a random configuration, the different rods aggregate inside the corresponding cavities. Long rods form a smectic monolayer which grows out of the substrate cavities.

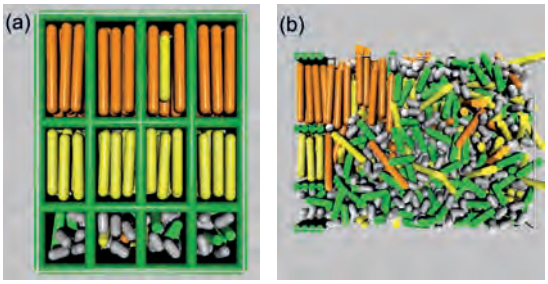


Fig. 3: Typical configurations for a system of rods with four different lengths in contact with a structured substrate with rectangular cavities of different sizes. Molecules demix and aggregate in the corresponding cavities as shown in (a) from the planar substrate (not shown) behind the cavities and (b) in a side view.

Low-Density Structures in Systems of Chemically Heterogenous Rods

Additional types of structures can form in systems of chemically heterogenous rods. We have studied rods with one or two short-range adhesive sites along the molecule axis which can adhere to sites of other rods **[4]**. Typical examples are stiff block-copolymers where the hydrophobic parts aggregate to screen themselves from the surrounding water. The chemically heterogenous rods form complex structures at rather low densities. Hard rods with one adhesive segment located halfway between the center and the end of the rod may form membrane-like clusters (**Fig. 4a**). For entropic reasons half of the rods point up and half point downward, resulting in a membrane of width $w \approx 3L/2$. If the adhesive segment is located at the end of the rods, micellar structures are formed (**Fig. 4b**).

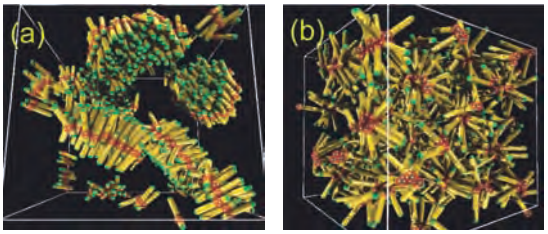


Fig. 4: Snapshots of hard rods with one adhesive segment (a) half way between the center and the end of the rod and (b) at the end of the rod.

The system behaves completely different if adhesive sites are located on both ends. For this type of rods with length $\lambda = 5$, we have estimated a phase diagram as a function of the reduced pressure P^* and the adhesive strength ε (**Fig. 5**). For small ε, the system shows an isotropic and a nematic state, just like a system of hard rods. For sufficiently large ε and low pressure a novel scaffold-like state is found with a flexible network of rods. The scaffold state is characterized by triangular structures formed by three mutually adhering rods. At higher pressures, small smectic-like bundles occur, before at even higher pressure a long-range smectic order sets in.

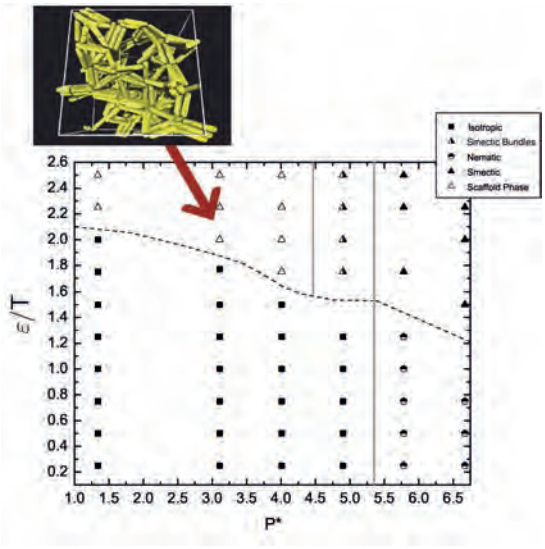


Fig. 5: Phase diagram of a system of hard rods with adhesive ends. For sufficiently high adhesion strength ε and low reduced pressure P the system forms a scaffold-like structure as shown in the snapshot on top.*

T. Gruhn, R. Chelakkot, E. Gutlederer, A. Richter.
thomas.gruhn@mpikg.mpg.de

References:

[1] Richter, A. and Gruhn, T.: Fractionation in polydisperse systems of spherocylindrical rods – The influence of attractive interactions and adjacent substrates, Mol. Phys. **104**, 3693-3699 (2006).
[2] Richter, A. and Gruhn, T.: Structure formation and fractionation in systems of polydisperse rods, J. Chem. Phys. **125**, 064908 (2006).
[3] Dogic, Z. and Fraden, S.: Development of model colloidal liquid crystals and the kinetics of the isotropic-smectic transition, Phil. Trans. R. Soc. Lond. A **359**, 997-1014 (2001).
[4] Chelakkot, R., Lipowsky, R., and Gruhn, T.: Novel low-density structure for hard rods with adhesive end-groups, Macromolecules **39**, 7138-7143 (2006).

Exploring Vesicle Fusion with Dissipative Particle Dynamics

Julian Charles Shillcock 18.10.1960
1982: B.Sc (Hons), Physics (Kings College London)
1985: M.Sc, Nuclear Physics (Simon Fraser University, Canada) Thesis: Hanbury-Brown Twiss Effect in Heavy-Ion Collisions
1986-1990: Research Scientist (British Aerospace, Space Systems Division, U.K.)
1995: PhD, Biophysics (Simon Fraser University, Canada) Thesis: Elastic Properties of Fluid and Polymerised Membranes under Stress
1995-1997: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
1998-1999: Senior Scientist (Molecular Simulations Inc., Cambridge, U.K.)
1999-2003: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
2004-2007: External Research Associate (Max Planck Institute of Colloids and Interfaces, Potsdam)

Computer models of biophysical processes are important both for understanding their generic features and for visualizing their dynamics **[1]**. Many interesting phenomena occur on length and time scales beyond the reach of traditional Molecular Dynamics (MD), and this has led to the development of so-called *mesoscopic* simulation methods. We have been using Dissipative Particle Dynamics (DPD) to construct improved models of amphiphilic membranes and explore the pathway of vesicle fusion. We have recently published an invited review of simulation methods applied to these soft matter systems **[2]**. Natural membranes, such as the cellular plasma membrane, are a complex mixture of many types of lipid molecule and protein. We have continued to study the material properties of amphiphilic membranes as models of lipid bilayers. The effects of molecular architecture **[3]** and a mixture of two molecule types with different tail lengths and intermolecular interactions **[4]** have been simulated using DPD (**Fig. 1**) by Gregoria Illya (now a post-doc at the MPI for Polymer Research in Mainz). The elastic properties of a membrane composed of two lipid species was also simulated **[5]** using coarse-grained Molecular Dynamics by Alberto Imparato (now a post-doc at the Politecnico di Torino in Torino, Italy). The two techniques produced similar results, indicating that the membrane properties are robust against changing the details of the simulation techniques.

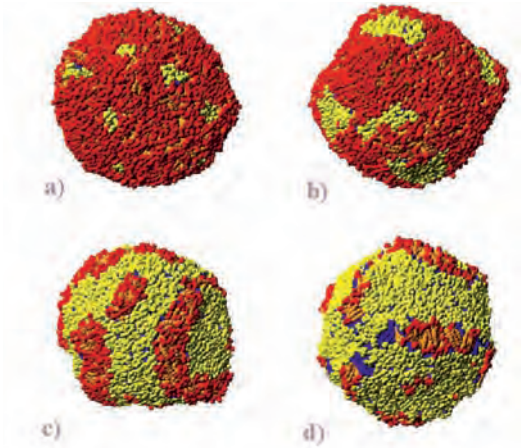


Fig. 1: Phase separation in a vesicle composed of two kinds of lipid with different hydrophobic tail lengths as a function of the longer-tailed lipid concentration (from [4]). The shape of the domains differs from those formed in planar bilayers containing the same lipid types and concentrations because the curvature of the vesicle influences the domain growth. The number fractions of the longer-tail lipid (shown with yellow heads) are as follows: a) 0.1, b) 0.3, c) 0.7, and d) 0.9. The shorter-tail lipids are shown with red heads.

A quite different class of vesicle-forming amphiphiles consists of diblock copolymers, such as poly(ethylene oxide)-polyethylethylene (PEO-PEE). These materials are important for applications such as drug delivery because they form vesicles that are more robust than lipid vesicles, and are not recognised as foreign by the human immune system. In collaboration with the groups of Professors M. Klein and D. Discher at the University of Pennsylvania, we have created a DPD model of PEO-PEE membranes and vesicles and calibrated the DPD parameters using MD simulations on smaller systems **[6]**. This illustrates one way of extending the more accurate, but far more computationally-expensive, MD technique to molecules and system sizes closer to biologically-relevant processes. One application, performed by the Discher group using our DPD code, is to the behaviour of stable pores in the nuclear membrane **[7]**.

Vesicle fusion is a vital cellular function, but the molecular rearrangements that occur when intact membranes approach, merge and fuse cannot yet be observed in experiments. We have extended our previous model **[8]** of tension-induced fusion in two independent ways. The first method replaces the global tensions in the membranes with local forces exerted by transmembrane barrel "proteins" that transduce forces into the membranes (**Fig. 2**).

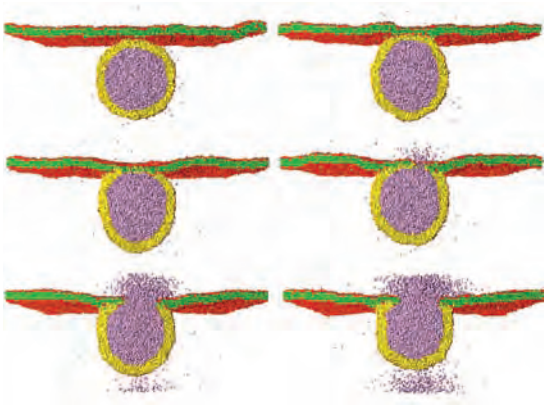


Fig. 2: Sequence of snapshots showing the fusion of a 28 nm diameter vesicle (yellow/orange beads) to a (100 nm)^2 planar membrane (green/red beads). Time proceeds across each row (from [2]). Both membranes are tensionless, and their fusion is driven by local forces exerted by membrane-spanning barrel "proteins". Six barrels are positioned in each membrane in an hexagonal arrangement. A specific force protocol is applied to the barrels to drive the membranes to fuse. After the system has equilibrated, oppositely-oriented bending moments are created in each membrane for 80 ns to bend them towards each other. When the membranes' proximal leaflets have touched, the bending moments are removed and the system is allowed to evolve for 32 ns in order for the two proximal leaflets to merge somewhat. An external force is then applied to the barrels in both membranes so as to raise the tension in the encircled contact zone. The force has a magnitude Fext = 0.4 k_BT/a_0 and is directed radially outward (a_0 is the bead diameter). It is applied in this instance for 64 ns. Once the pore has appeared, it initially expands under the pressure of the inner solvent flowing outwards, but as the membrane relaxes back to its tensionless state it shrinks.

The second method retains the global tensions as the control parameters, and uses a systematic exploration of new parameter sets to develop a more accurate representation of the membrane's mechanical properties (**Fig. 3**). One such parameter set **[9]** was introduced by Lianghui Gao (a post-doc now in Beijing, China) and shows that finite-size effects must be carefully assessed before the model can be compared with experimental systems. This result is important for the development of simulations of many soft matter systems. Lianghui Gao and Andrea Grafmüller, a PhD student, have independently produced two new membrane parameter sets that reveal more details about the pathway of tension-induced vesicle fusion. Key features of these parameter sets are that the membrane is less stretchable than before, and the relation between its tension and area per molecule is linear over the whole range of tensions for which the membrane is intact.

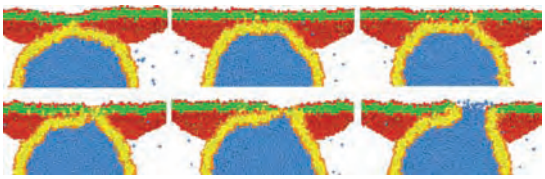


Fig. 3: Fusion pathway of a 30 nm diameter vesicle (yellow/orange beads) to a (50 nm)^2 planar membrane (green/red beads) driven by tension. Time proceeds across each row (from [10]). The stages of fusion are: adhesion of vesicle to membrane (snapshot 2); flip-flop of lipids from the vesicle to the planar membrane (snapshot 3); formation of a disordered, irregularly-shaped contact zone (snapshot 4); transformation of part of the contact zone into a hemifused lamella state (snapshot 5); rupture of the hemifused patch and growth of the fusion pore (snapshot 6).

Andrea Grafmüller has used one of the new parameter sets **[10]** to simulate the fusion of a vesicle to a planar membrane (**Fig. 3**). Both small, 15 nm diameter, and large, 30 nm diameter, vesicles have been followed as they interact with a planar membrane patch that is 50 x 50 nm^2. These simulations have revealed that the fusion of a relaxed vesicle to a tense membrane passes through two energy barriers. The first corresponds to the time required for individual lipid molecules to flip-flop from the (relaxed) vesicle to the (tense) planar membrane; and the second to the appearance of the fusion pore in a bean-shaped disordered region created by the mingling of vesicle and planar membrane lipids. This result may be important for interpreting fusion experiments as most theoretical models to date assume a single energy barrier in the fusion pathway.

J. C. Shillcock, L. Gao, A. Grafmüller, R. Lipowsky.
Julian.Shillcock@mpikg.mpg.de

References:

[1] Shillcock, J. C. and Lipowsky, R. Visualizing soft matter: mesoscopic simulations of membranes, vesicles and nanoparticles. Biophys. Reviews and Letters, Vol 2 No.1, 33-55 (2007).
[2] Shillcock, J. C. and Lipowsky, R. The computational route from bilayer membranes to vesicle fusion. J. Phys. Cond. Mat. **18**, S1191-S1219 (2006).
[3] Illya, G., Lipowsky, R. and Shillcock, J. C. Effect of chain length and asymmetry on material properties of bilayer membranes. J. Chem. Phys. **122**, 244901-1-244901-6 (2005).
[4] Illya, G., Lipowsky, R., and Shillcock, J. C. Two-component membrane material properties and domain formation from dissipative particle dynamics. J. Chem. Phys. **125**, 114710-1-114710-9 (2006).
[5] Imparato, A., Shillcock, J. C. and Lipowsky, R. Shape fluctuations and elastic properties of two-component bilayer membranes. Europhys. Lett. **69**, 650-656 (2005).
[6] Ortiz, V., Nielsen, S. O., Discher, D. E, Klein, M. L., Lipowsky, R., and Shillcock, J. C. Dissipative particle dynamics simulations of polymersomes. J. Phys. Chem. B **109**, 17708-17714 (2005).
[7] Photos, P. J., Bermudez, H., Aranda-Espinoza, H, Shillcock, J. C. and Discher D. E. Nuclear pores and membrane holes: generic models for confined chains and entropic barriers in pore stabilization. Soft Matter **3**, 1-9 (2007).
[8] Shillcock, J. C. and Lipowsky, R. Tension-induced fusion of membranes and vesicles. Nature Materials **4**, 225-228 (2005).
[9] Gao, L., Shillcock, J. C. and Lipowsky, R. Improved dissipative particle dynamics simulations of lipid bilayers. J. Chem. Phys. (accepted 2006).
[10] Grafmüller, A., Shillcock, J. C. and Lipowsky, R. Pathway of membrane fusion with two energy barriers. Phys. Rev. Lett. (accepted 2007).

Unveiling Membrane Fusion

Rumiana Dimova 06.04.1971
1995: Diploma, Chemistry (Sofia University, Bulgaria), Major: Chemical Physics and Theoretical Chemistry, Thesis: Role of the Ionic-Correlation and the Hydration Surface Forces in the Stability of Thin Liquid Films
1997: Second MSc (Sofia University, Bulgaria) Thesis: Interactions between Model Membranes and Micron-Sized Particles
1999: PhD, Physical Chemistry (Bordeaux University, France) Thesis: Hydrodynamical Properties of Model Membranes Studied by Means of Optical Trapping Manipulation of Micron-Sized Particles
2000: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2001: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Membrane fusion is an essential and ubiquitous cellular process. It is involved, for example, in cellular secretion via exocytosis, signalling between nerve cells, and virus infection. In both the life sciences and bioengineering, controlled membrane fusion has many possible applications, such as drug delivery, gene transfer, chemical microreactors, or synthesis of nanomaterials. While previous studies have explored many of the steps involved in membrane fusion, the efforts to fully understand the dynamics of membrane fusion have been stymied by the speed with which this process occurs.

Recently, our lab has succeeded in the development of two independent methods of initiating the fusion process in a controlled manner. This, in turn enabled us to observe the subsequent fusion dynamics, using phase contrast microscopy and a fast digital camera, with a temporal resolution in the microsecond range **[1]**. This time resolution is unprecedented, as direct observations of fusion in the literature access only times larger than several milliseconds.

The fusion process was observed on giant unilamellar vesicles (~ several tens of micrometers in diameter). In the first protocol **[2]**, the vesicles were functionalized with synthetic fusion-triggering molecules (β-diketonate ligands). Then, two of these liposomes were aspirated into two glass micropipettes. Membrane fusion was subsequently induced by the local addition of ions that form a complex between two fusogenic molecules embedded in the opposing membranes; see **Fig. 1**.

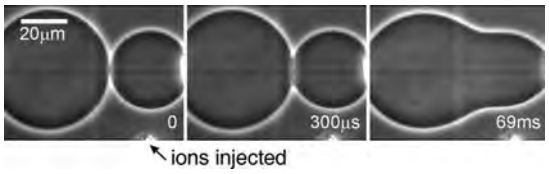


Fig. 1: Snapshots from the fusion of two functionalized vesicles held by micropipettes (only the right pipette tip is visible on the snapshots). A third pipette (bottom right corner) is used to inject a small volume (few tens of nanoliters) of solution of $EuCl_3$ which triggers the fusion. The time after the beginning of the fusion process is indicated in the lower right corner.

In the second protocol, two lipid vesicles were brought into contact by weak alternating electric fields. The AC field served to line up the vesicles along the direction of the field. Thus, while the micropipettes were used to manipulate the vesicles in the first protocol, the AC field was the manipulation tool in the second one. Once close contact was established, membrane fusion was induced by exposing the vesicles to a strong electric pulse. Such a pulse leads to the formation of membrane pores **[3]** in the opposing membranes, which subsequently fuse in order to dispose of the edges of the pores. In the presence of salt in the vesicle exterior, the vesicles deform to acquire cylindrical shapes with round caps **[4]**. In the absence of salt, this curious deformation is not observed, and multiple fusion necks are formed in contrast to the no-salt case where a single fusion neck is formed; see **Fig. 2**.

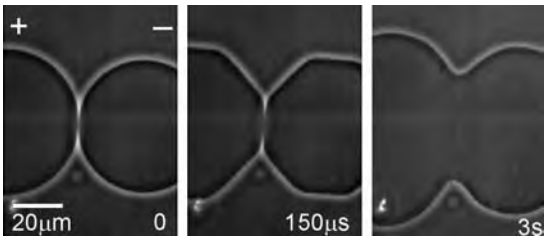


Fig. 2: Snapshot series from the electrofusion of two vesicles. The polarity of the electrodes is indicated with a plus (+) or a minus (-) sign on the first snapshot. The amplitude of the pulse was 150 V (3 kV/cm), and its duration was 150 μs. The starting time t = 0 corresponds to the beginning of the pulse. The image acquisition rate was 20 000 frames per second. The external vesicle solution contained 1 mM NaCl, which causes the flattening of the vesicle membrane and induce cylindrical deformation [4].

With either method, ligand mediated fusion or electrofusion, the process was recorded using a fast digital camera with an acquisition rate of 20 000 frames per second, corresponding to a temporal resolution of 50 microseconds. This constitutes a 1000-fold improvement compared to other direct-observation microscopy reports on fusion. The direct imaging provided by the two fusion protocols and the fast acquisition speed confirmed that the fusion process is extremely fast, and offered some insight into the dynamics of the process. The improved temporal resolution suggests that for the formation of a fusion neck, the cell needs only a few hundred nanoseconds. Within 50 microseconds, the fusion neck connecting the two vesicles was observed to have already reached a diameter of a few micrometers **[1]**. This suggests that the opening of the fusion pore occurs with an expansion velocity of a few centimeters per second. The experimental data could be extrapolated to shorter times covered by simulation studies performed in our department. The latter nicely support the conjecture that fusion times are on the order of 200 nanoseconds.

Having demonstrated the potential of the method for controlling and imaging membrane fusion, we applied it to a slightly more sophisticated system. Namely, we fused two vesicles whose membranes were composed of different lipids (Dioleoylphosphocholine and Sphingomyelin) and cholesterol. At a certain temperature, these lipids form fluid phases, also known as liquid ordered and liquid disordered. These phases are immiscible and the liquid ordered phase, which is stabilized by cholesterol, is thought to mimic rafts in cell membranes.

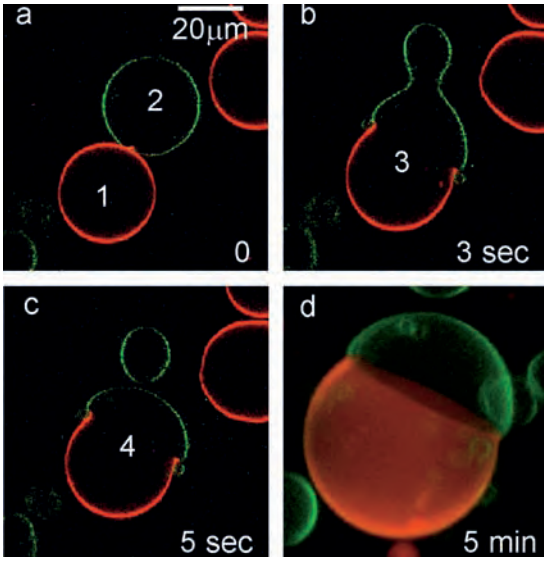


Fig. 3: Creating a multidomain vesicle by electrofusion of two vesicles of different composition as observed with fluorescence microscopy. The images (a-c) are acquired with confocal microscopy scans nearly at the equatorial plane of the fusing vesicles. (a) Vesicle 1 is composed of Dioleoylphosphocholine:Cholesterol (8:2) and labeled with the fluorescent dye DiI-C_{18} (red). Vesicle 2 is made of Sphingomyelin:Cholesterol (7:3) and labeled with the fluorescent dye perylene (green). (b) The two vesicles were subjected to an electric pulse of strength 300 V (6 kV/cm) and duration 300 μs. Vesicles 1 and 2 have fused to form vesicle 3. (c) Right after the fusion, the Sphingomyelin:Cholesterol part (green) begins to bud forming a small daughter vesicle. (d) A three-dimensional image projection of vesicle 4.

When two such vesicles are forced to fuse, the resulting vesicle contains two or more domains. We used the electrofusion protocol to form these multidomain vesicles **[5]**. The fusion products were explored using confocal microscopy, see **Fig. 3**. Having the tool to form these domains on vesicles in a controlled fashion would allow us to study their stability at various conditions like temperature and membrane tension (PhD project of Natalya Bezlyepkina).

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. Being able to control fusion, we used our approach to form multidomain vesicles and study the stability of the domains. Currently we apply the electrofusion of giant vesicles as a tool to create microreactors with very small volumes (postdoctoral project of Peng Yang). The vesicles used in the present study were only tens of microns in size. Fusing two of these vesicles of different content would be equivalent to performing a reaction in a tiny volume of some picoliters, which would be advantageous for synthesis of nanomaterials. Furthermore, vesicles as microscopic vessels loaded with polymer solutions can be used to study phase separation in confined systems (PhD project of Yanhong Li), which mimics microcompartmentation in cells.

R. Dimova, N. Bezlyepkina, C. Haluska,
Y. Li, K. A. Riske, P. Yang
Rumiana.Dimova@mpikg.mpg.de

References:

[1] Haluska, C. K., Riske, K. A., Marchi-Artzner, V., Lehn, J.-M., Lipowsky R. and Dimova, R.: Timescales of membrane fusion revealed by direct imaging of vesicle fusion with high temporal resolution. Proc. Natl. Acad. Sci. USA. **103**, 15841-15846 (2006).

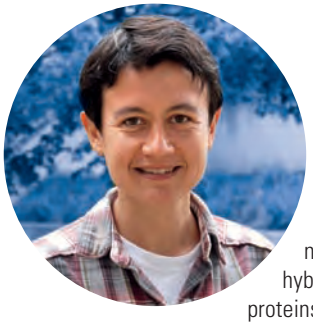
[2] Haluska, C. K.: Interactions of functionalized vesicles in the presence of Europium (III) Chloride. PhD Thesis, (2005).

[3] Riske, K. A. and Dimova, R.: Electro-deformation and -poration of giant vesicles viewed with high temporal resolution. Biophys. J., **88**, 1143-1155 (2005).

[4] Riske, K. A. and Dimova, R.: Electric pulses induce cylindrical deformations on giant vesicles in salt solutions. Biophys. J. **91**, 1778-1786 (2006).

[5] Riske, K. A., Bezlyepkina, N., Lipowsky, R. and Dimova, R.: Electrofusion of model lipid membranes viewed with high temporal resolution. Biophys. Rev. Lett. **4**, 387-400 (2006).

Electro-Deformation and -Poration of Vesicles



Rumiana Dimova 06.04.1971
1995: Diploma, Chemistry (Sofia University, Bulgaria), Major: Chemical Physics and Theoretical Chemistry, Thesis: Role of the Ionic-Correlation and the Hydration Surface Forces in the Stability of Thin Liquid Films
1997: Second MSc (Sofia University, Bulgaria) Thesis: Interactions between Model Membranes and Micron-Sized Particles
1999: PhD, Physical Chemistry (Bordeaux University, France) Thesis: Hydrodynamical Properties of Model Membranes Studied by Means of Optical Trapping Manipulation of Micron-Sized Particles
2000: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2001: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

The response of membranes to electric fields has been extensively studied in the last decades. The phenomena of electrodeformation, electroporation and electrofusion are of particular interest because of their widespread use in cell biology and biotechnology as means for cell manipulation, cell hybridization or for introducing molecules such as proteins, foreign genes (plasmids), antibodies, or drugs into cells. Giant vesicles are the simplest model of the cell membrane. Being of cell size, they are convenient for direct microscopy observations.

Deformation in AC Fields

When subjected to alternating electric fields, giant vesicles deform into elliptical shapes. The deformation depends on the AC field frequency and on the conductivities of the aqueous solution in the interior and exterior vesicle compartments **[1]**. When the interior solution has conductivity (σ_{in}) higher than the exterior one (σ_{out}), a quasispherical vesicle deforms into a prolate. This deformation is observed for a large range of AC frequencies, up to 10^6 Hz. Interestingly, whenever the internal conductivity is lower than the external one ($\sigma_{in} < \sigma_{out}$), as in **Fig. 1**, a prolate-oblate transition (**Fig. 1a** and **1b**) is observed for intermediate frequencies of a few kHz. This applies also to external conductivities close to physiological conditions. At higher frequencies, more than about 10^7 Hz, the vesicles attain a spherical shape (**Fig. 1c**) irrespective of conductivity conditions; see **Fig. 2**.

Fig. 1: A giant vesicle (phase contrast microscopy) subjected to an AC field of 10 V (2 kV/cm). The field direction is indicated with the arrow in (a). The external solution has a higher conductivity than the internal one ($\sigma_{in} > \sigma_{out}$). From (a) to (c) the field frequency increases causing shape transformations of the vesicle: (a) 5 kHz, prolate morphology; (b) 100 kHz, oblate shape; (c) 10 MHz, sphere.

Using giant unilamellar vesicles made of egg PC, we succeeded to map the morphological transitions as a function of AC frequency and conductivity ratios. The conductivities were varied by the addition of NaCl (leading to concentration of up to about 1 mM) in the exterior or interior vesicle solutions. A large interval of frequencies was studied (up to 10^8 Hz). The degree of vesicle deformation was quantitatively characterized from optical video microscopy images.

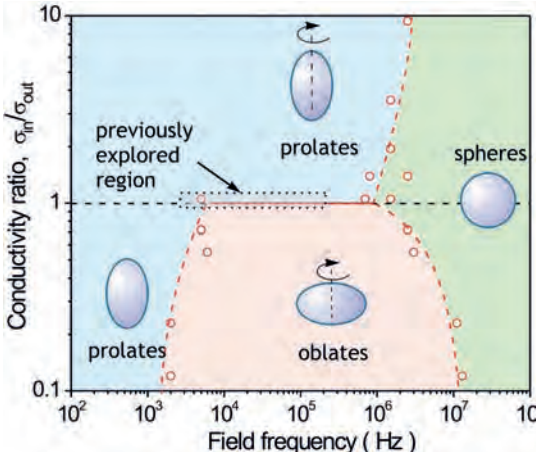


Fig. 2: Morphological diagram of the shape transformations of vesicles in different conductivity conditions and various field frequencies. When the conductivity of the solution inside the vesicles is larger than the one outside, ($\sigma_{in} > \sigma_{out}$), transitions from prolate to spherical vesicles are observed (upper part of the diagram). For internal conductivities lower than the external one ($\sigma_{in} > \sigma_{out}$), the vesicle undergoes prolate-to-oblate-to-sphere transitions depending on the field frequency (lower part of the diagram). The open circles are experimentally determined. The dashed lines are guides to the eye for the various region boundaries. The area surrounded by the dotted line shows the region previously explored in the literature.

Earlier studies by Helfrich and collaborators (see e.g. Winterhalter and Helfrich, *J. Coll. Interf. Sci.* 122, 1987) report on prolate deformations of vesicles in AC fields, but conductivity asymmetry has not been studied and thus not taken into account in the theoretical modelling. Thus the transition observed in our system cannot be predicted by the existing theory. We extended these theories to include the effect of asymmetric conductivity conditions and the frequency dependence of the conductivity (PhD project of Said Aranda).

Electroporation of Vesicles Subjected to DC Pulses

When subjected to short and strong electric pulses (~100 µs, ~1 kV/cm) the vesicle response is qualitatively similar to the one in AC fields. However, microscopy observation of effects caused by electric pulses on giant vesicles is difficult because of the short duration of the pulses. To tackle this problem, recently in our group, imaging with a fast digital camera was used to record the pulse response of giant lipid vesicles with a high temporal resolution of up to 30 000 frames per second (one image every 33 microseconds) **[2]**. This approach helped record extraordinary cylindrical shapes on vesicles **[3]**. These unusual morphologies (cylinders or disks with spherical caps) have not been previously observed due to their short lifetime of a few milliseconds. The observation with the fast digital camera allowed resolving the pores on the vesicle and the dynamics of the vesicle response **[2]**. The lifetime of the pores, which was in the millisecond range, was found to depend on the membrane viscosity. In the fluid phase, the latter can be determined from optical manipulation of a probe attached to the membrane (optical dynamometry) **[4]**. When the membrane undergoes a fluid-to-gel transition, the membrane viscosity drastically increases. Thus, it is to be expected that the lifetime of pores formed on vesicles in the gel phase would be much longer. We attempted to visualize such pores using confocal microscopy on giant vesicles in the gel phase; see **Fig. 3**. Indeed, the time of these pores to reseal was orders of magnitude longer than the lifetime of pores in electroporated membranes in the fluid phase **[5]**.

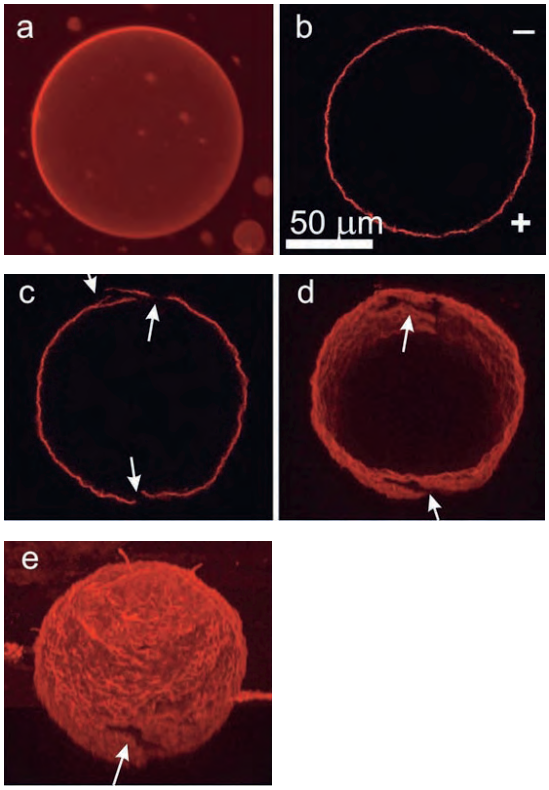


Fig. 3: Electroporation of a fluorescently labeled vesicle in the gel phase as imaged with confocal microscopy. (a) A 3d projection averaged image of a vesicle in the fluid phase. (b-e) Images of a vesicle in the gel phase: Equatorial sections of the vesicle before (b) and after poration (c) caused by an electric pulse of 300 V (6 KV/cm) and duration 300 microseconds. The electrode polarity is indicated with plus (+) and minus (-) signs in (b). The arrows in (c) show the ruptured zones at the vesicle poles. A 30 micrometer wide stripe from the equatorial area of the vesicle (slightly rotated around the horizontal axis) shows the ruptured places in the membrane at the north and south poles (d) as indicated with arrows. A complete 3d projection average image of the same vesicle (again rotated around the x-axis) shows better the crack on the southern pole of the vesicle (e) pointed by the arrow. Contrary to vesicles in the fluid phase (a), pores formed on vesicles in the gel phase (e) do not reseal over a period of at least ten minutes.

R. Dimova, S. Aranda, R. Knorr, K. A. Riske
Rumiana.Dimova@mpikg.mpg.de

References:

[1] Dimova, R., Aranda, S., Bezlyepkina, N., Nikolov, V., Riske, K. A. and Lipowsky, R.: A practical guide to giant vesicles. Probing the membrane nanoregime via optical microscopy. J. Phys.: Condens. Matter, **18**, S1151-S1176 (2006).
[2] Riske, K. A. and Dimova, R.: Electro-deformation and -poration of giant vesicles viewed with high temporal resolution. Biophys. J., **88**, 1143-1155 (2005).
[3] Riske, K. A. and Dimova, R.: Electric pulses induce cylindrical deformations on giant vesicles in salt solutions. Biophys. J. **91**, 1778-1786 (2006).
[4] Dimova, R. and Pouligny, B.: Optical dynamometry to study phase transitions in lipid membranes. in "Protocols in Biophysics to Study Membrane Lipids", ed. A. Dopico, Humana Press, in press.
[5] Dimova, R., Aranda, S., Riske, K. A., Knorr, R. and Lipowsky, R.: Vesicles in electric fields, in preparation.

Molecular Recognition in Membrane Adhesion

Thomas Weikl 01.04.1970
1996: Diploma, Physics
(Freie Universität Berlin)
Thesis: Interactions of rigid membrane inclusions
1999: PhD, Physics
(Max Planck Institute of Colloids and Interfaces, Potsdam)
Thesis: Adhesion of multicomponent membranes
2000-2002: Postdoc
(University of California, San Francisco)
Since 2002: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

Cells adhere to other cells via adhesion molecules located on their membrane surfaces. Each adhesion molecule on one cell binds to a "partner molecule" on the other cell. The two binding partners can be identical molecules, like two hands holding each other, or distinct molecules that fit together like a lock and a key. Cadherins, for example, are adhesion molecules that often bind to identical cadherins, holding together cells of the same type in the development and maintenance of body tissues. Integrins and selectins, on the other hand, bind to distinct adhesion partners, for example during adhesion of white blood cells in an immune defense.

The adhesion of two cells involves a subtle balance between the attractive binding energies of the adhesion molecules and repulsive energies, which result from cell shape fluctuations or from large non-adhesive proteins that impede adhesion. In a healthy organism, cells have to control this balance between attraction and repulsion. For some cancers, mutations of adhesion molecules shift the balance and lead to abnormal cell-cell adhesion events and tumor growth.

Active Switching of Adhesion Molecules

Via gene expression, cells can regulate the numbers and types of adhesion molecules at their surfaces and, thus, the strength and specifity of their adhesiveness. But some cells are known to change their adhesiveness rather quickly, much more quickly than gene expression allows. These cells have adhesion molecules that can be switched between different states. Integrins, for example, are adhesion molecules that have at least two different conformational states. In a "stretched" conformational state, the integrins are active and can bind to their partners on an apposing cell surface. In a "bent" state, the integrins are inactive and can't bind (see **Fig. 1**).

The numbers of active integrins are crucial for the adhesiveness of these cells. But besides mere numbers, other effects may count as well. We have shown that the characteristic switching rates of adhesion molecules can strongly affect the adhesiveness. The switching of an adhesion molecule between an active and an inactive conformation is a stochastic process, i.e. a process that occurs with a certain probability at a certain time. The process typically requires the input of "chemical energy", e.g., from ATP molecules, at least in one direction.

We have thus studied the adhesion of membranes via switchable adhesion molecules **[1, 2, 3]**. The two opposing forces in the adhesion balance of the membranes are the attractive forces of the adhesion molecules, and repulsive forces from membrane shape fluctuations. Both forces have characteristic times scales. These time scales are the switching times of the adhesion molecules, and the relaxation times of the membrane shape fluctuations. A resonance effect occurs if the characteristic times are similar (see **Fig. 1**). The resonance leads to an increase in membrane fluctuations, and to a decrease of the adhesiveness of the membranes **[1, 3]**.

This resonance effect may also be used to control cell adhesion. During the last decade, synthetic molecules have been developed that can be switched by light between different conformations. The switching times of such molecules depend on the light intensity. Anchored at a substrate, the molecules can be used to switch the adhesive substrate properties and, thus, to manipulate and study cell adhesion.

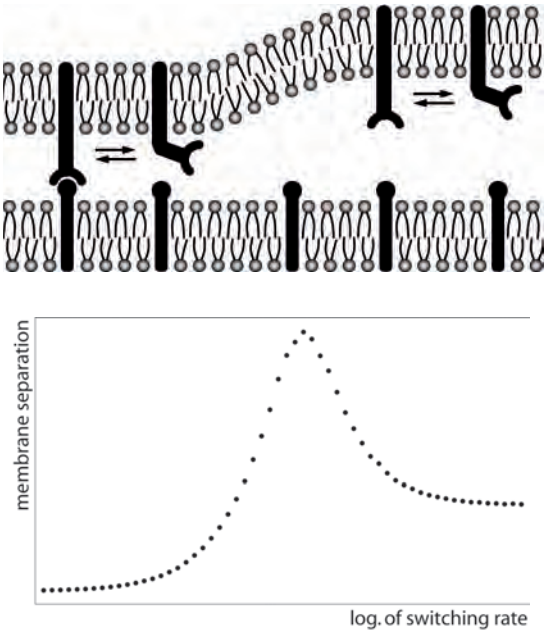


Fig. 1: (Top) A membrane with switchable adhesion molecules adhering to a second membrane. The adhesion molecules are switched between a stretched, active conformation and a bent, inactive conformation. In the stretched conformation, the adhesion molecules can bind to their ligands in the other membrane. (Bottom) Membrane separation as a function of the receptor switching rate. The active switching leads to a stochastic resonance with increased membrane separations at intermediate switching rates.

Long and Short Adhesion Molecules

The adhesion of biological membranes often involves various types of adhesion molecules. These adhesion molecules can have different lengths. The adhesion molecule complexes that mediate the adhesion of T cells, for example, have characteristic lengths of 15 or 40 nm. During T cell adhesion, a lateral phase separation into domains that are either rich in short or long adhesion molecules occurs. The domain formation is presumably caused by the length mismatch of the adhesion molecules **[4]**. The domains may play a central role for T cell signaling in immune responses.

We have developed a statistical-mechanical model for membranes interacting via various types of adhesion molecules **[4, 5]**. In our model, the membranes are discretized into small patches that can contain single adhesion molecules. The conformations of the membranes are characterized by the local separation of apposing membrane patches, and by the distribution of adhesion molecules in the membranes.

The equilibrium phase behavior of the membranes can be derived from the partition function of our model. The partition function is the sum over all possible membrane conformations, weighted by their Boltzmann factors. In our model, the summation over all possible distributions of the adhesion molecules in the partition function leads to an effective double-well potential (see **Fig. 2**). The depths of the wells depend on the concentrations and binding energies of the molecules.

The membranes exhibit two characteristic phase transitions. The first transition is the unbinding transition of the membranes, which is driven by an entropic membrane repulsion arising from thermal shape fluctuations. The second transition is lateral phase separation within the membranes, driven by the length mismatch of the adhesion molecules. The length mismatch leads to a membrane-mediated repulsion between long and short adhesion molecules, because the membranes have to be bent to compensate this mismatch, which costs elastic energy. This repulsion leads to a lateral phase separation for sufficiently large concentrations of the molecules and, thus, sufficiently deep wells of the effective potential (see **Fig. 3**).

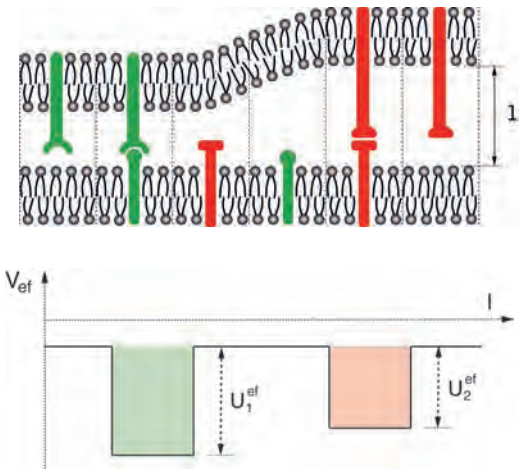


Fig. 2: (Top) A membrane containing long and short receptor molecules (upper membrane) adhering to a membrane with complementary ligands. (Bottom) The effective adhesion potential V_{ef} of the membranes is a double-well potential. The potential well at short separations l reflects the interactions of the short receptor/ligand bonds, the well at larger separations reflects the interactions of the long receptor/ligand bonds.

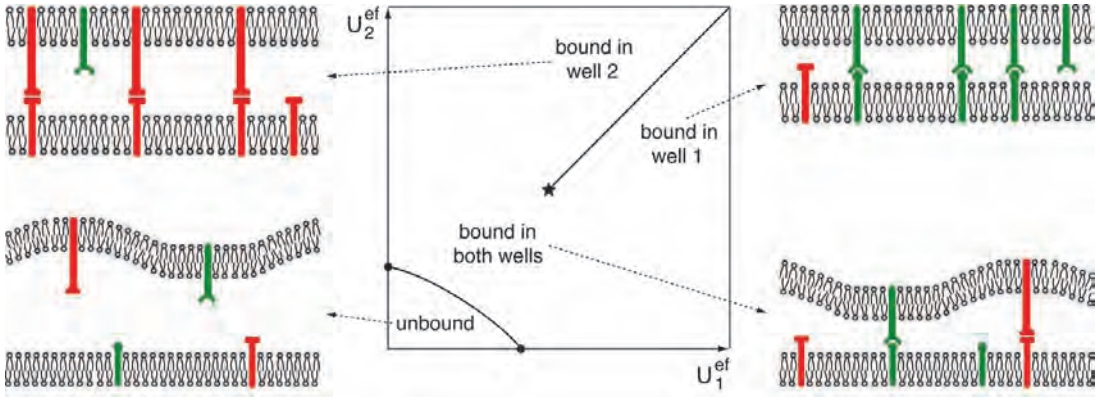


Fig. 3: Phase diagram of membranes adhering via long and short adhesion molecules. The membranes are unbound for small well depths U_1^{ef} and U_2^{ef} of the effective interaction potential shown in Fig. 2, i.e. for small concentrations or binding energies of receptors and ligands. At large values of U_1^{ef} and U_2^{ef}, the membranes are either bound in well 1 or well 2. At intermediate well depths, the membranes are bound in both potential wells.

T. Weikl, M. Asfaw, H. Krobath, B. Rozycki, R. Lipowsky
thomas.weikl@mpikg.mpg.de

References:

[1] Rozycki, B., Lipowsky, R., and Weikl, T. R.: Adhesion of membranes with active stickers. Phys. Rev. Lett. **96**, 048101 (2006).

[2] Rozycki, B., Weikl, T. R, and Lipowsky, R.: Adhesion of membranes via switchable molecules. Phys. Rev. E. **73**, 061908 (2006).

[3] Rozycki, B., Weikl, T. R, and Lipowsky, R.: Stochastic resonance for adhesion of membranes with active stickers. Eur. Phys. J. E, in press.

[4] Weikl, T. R., and Lipowsky, R.: Pattern formation during T cell adhesion. Biophys. J. **87**, 3665-3678 (2004).

[5] Asfaw, M., Rozycki, B., Lipowsky, R., and Weikl, T. R.: Membrane adhesion via competing receptor/ligand bonds. Europhys. Lett. **76**, 703-709 (2006).

Activity Patterns on Scale-Free Networks

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)

The biosphere contains many complex networks built up from rather different elements such as molecules, cells, organisms, or machines. In spite of their diversity, these networks exhibit some univeral features and generic properties. The basic elements of each network can be represented by nodes or vertices. Furthermore, any binary relation between these elements can be described by connections or edges between these vertices as shown in **Fig. 1**. By definition, the degree k of a given vertex is equal to the number of edges connected to it, i.e., to the number of direct neighbors. Large networks containing many vertices can then be characterized by their degree distribution, P(k), which represents the probability that a randomly chosen vertex has degree k.

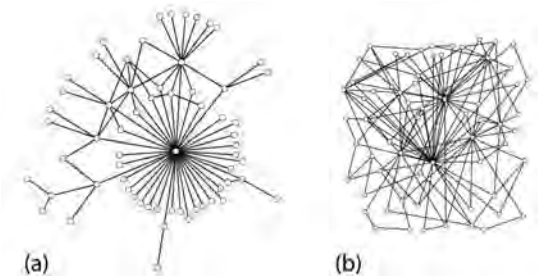


Fig. 1: Two examples for small scale-free networks: (a) Network with scaling exponent $\gamma = 2$ and minimal degree $k_0 = 1$. This network has a tree-like structure and a small number of closed cycles; and (b) Network with scaling exponent $\gamma = 5/2$ and minimal degree $k_0 = 2$ for which all edges belong to closed cycles.

Scale-Free Degree Distributions

Many biological, social, and technological networks are found to be scale-free in the sense that their degree distribution decays as

$$P(k) \sim 1/k^{\gamma} \text{ for } k > k_0$$

which defines the scaling exponent γ. Typical values for this exponent are found to lie between 2 and 5/2. **[1,2]** As one would expect naively, there are fewer vertices with a larger number of connections. However, since the probability P(k) decreases rather slowly with k, a large network with many vertices always contains some high-degree vertices with a large number of direct neighbors.

As an example, let us consider neural networks. The human brain consists of about 100 billion nerve cells or neurons that are interconnected to form a huge network. Each neuron can be active by producing an action potential. If we were able to make a snapshot of the whole neural network, we would see, at any moment in time, a certain pattern of active and inactive neurons. If we combined many such snapshots into a movie, we would find that this activity pattern changes continuously with time. At present, one cannot observe such activity patterns on the level of single neurons, but modern imaging techniques enable us to monitor coarse-grained patterns with a reduced spatial resolution. Using functional magnetic resonance imaging, for example, we can obtain activity patterns of about 100 000 neural domains, each of which contains about a million neurons.

These neural domains form another, coarse-grained network. Each domain corresponds to a vertex of this network, and each vertex can again be characterized by its degree k, i.e., by the number of connections to other vertices. It has been recently concluded from magnetic resonance images that the functional networks of neural domains are scale-free and characterized by a degree distribution with scaling exponent $\gamma = 2.1$.

Dynamical Variables and Activity Patterns

In general, the elements of real networks are dynamic and exhibit various properties that change with time. A more detailed description of the network is then obtained in terms of dynamical variables associated with each vertex of the network. In many cases, these variables evolve fast compared to changes in the network topology, which is therefore taken to be time-independent. Two examples for such dynamical processes are provided by neural networks that can be characterized by firing and nonfiring neurons or by the regulation of genetic networks that exhibit a changing pattern of active and inactive genes. In these examples, each dynamical variable can attain only two states (active or inactive), and the configuration of all of these variables defines the activity pattern of the network as shown in **Fig. 2**.

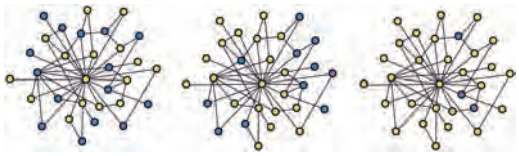


Fig. 2: Three subsequent snapshots of the activity pattern on a small scale-free network with 31 vertices and 50 edges. The active and inactive vertices are yellow and blue, respectively. For the initial pattern on the left, about half of the vertices are inactive (blue); for the final pattern on the right, almost all vertices are active (yellow). Each vertex of the network has a certain degree which is equal to the number of connections attached to it; this number is explicitly given for some nodes on the left.

Local Majority Rules Dynamics

In collaboration with Haijun Zhou (now professor at ITP, CAS, Beijing), we have recently started to theoretically study the time evolution of such activity patterns. **[3,4]** We focused on the presumably simplest dynamics as generated by a local majority rule: If, at a certain time, most direct neighbors of a certain vertex are active or inactive, this vertex will become active or inactive at the next update of the pattern. This dynamical rule leads to two fixed points corresponding to two completely ordered patterns, the all-active pattern and the all-inactive one. Each fixed point has a basin of attraction consisting of all patterns that evolve towards this fixed point for sufficiently long times. The boundary between the two basins of attraction of the two fixed points represents the so-called separatrix. One global characterization of the space of activity patterns is the distance of a fixed point from the separatrix as measured by the smallest number of vertices one has to switch from active to inactive (or vice versa) in order to reach the basin of attraction of the other fixed point.

Distance Between Fixed Points and Separatrix

We found that, for scale-free networks, this distance corresponds to selective switches of the high-degree vertices and strongly depends on the scaling exponent γ. For a network with N vertices, the number Ω of highly connected vertices that one has to switch in the all-active (or all-inactive) pattern in order to perturb this pattern beyond the separatrix grows as $\Omega = N/2^{\zeta}$ with $\zeta = (\gamma-1)/(\gamma-2)$ and vanishes as an essential singularity when the scaling exponent γ approaches the value $\gamma = 2$ from above. **[3]** If we used random rather than selective switches, on the other hand, we would have to switch of the order of N/2 vertices irrespective of the value of γ. Note that, in the limit in which the scaling exponent γ becomes large, selective and random switching lead to the same distance Ω. A low-dimensional cartoon of the high-dimensional pattern space is shown in **Fig. 3**.

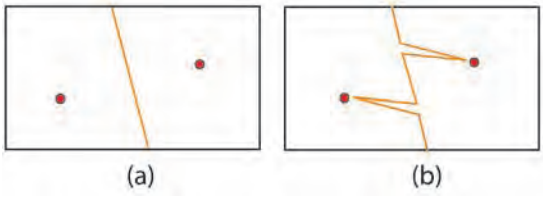


Fig. 3: Two fixed points (red dots) and separatrix (orange line) between their basins of attraction; (a) For large values of the scaling exponent γ the separatrix is smooth; (b) As the scaling exponent is decreased towards the value $\gamma = 2$, the separatrix develops spikes which come very close to the fixed points. These spikes correspond to the selective switching of the high-degree vertices.

Decay Times of Disordered Patterns

Another surprising feature of activity patterns on scale-free networks is the evolution of strongly disordered patterns that are initially close to the separatrix. These patterns decay towards one of the two ordered patterns but the corresponding decay time, i.e., the time it takes to reach these fixed points, again depends strongly on the scaling exponent γ.

We have developed a mean field theory that predicts qualitatively different behavior for $\gamma < 5/2$ and $\gamma > 5/2$. **[3,4]** For $2 < \gamma < 5/2$, strongly disordered patterns decay within a finite decay time even in the limit of infinite networks. For $\gamma > 5/2$, on the other hand, this decay time diverges logarithmically with the network size N. These mean field predictions have been checked by extensive computer simulations of two different ensembles of random scale-free networks using both parallel (or synchronous) as well as random sequential (or asynchronous) updating. **[4]** The two ensembles consist of (i) multi-networks that typically contain many self-connections and multiple edges and (ii) simple-networks without self-connections and multiple edges. For simple-networks, the simulations confirm the mean field results, see **Fig. 4**. For multi-networks, it is more difficult to determine the asymptotic behavior for large number of vertices since these networks are governed by an effective, N-dependent scaling exponent γ_{eff} that exceeds γ for finite values of N. **[4]**

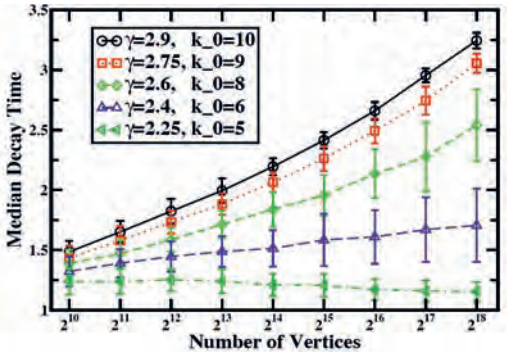


Fig. 4: Decay times for strongly disorderd patterns as a function of the number, N, of vertices contained in simple-networks for random sequential updating. The minimal vertex degree k_0 was chosen in such a way that the average degree is roughly equal for all values of the scaling exponent γ. In the limit of large N, the decay times attain a finite value for $\gamma < 5/2$ but increase logarithmically with N for $\gamma > 5/2$.

R. Lipowsky, J. Menche, A. Valleriani
reinhard.lipowsky@mpikg.mpg

References:

[1] Albert, R. and Barabasi, A.-L.: Statistical mechanics of complex networks. Rev. Mod. Phys. **74**, 47 (2002).
[2] Newman, M. E. J.: The structure and function of complex networks. SIAM Review **45**, 167 (2003).
[3] Zhou, H., and Lipowsky, R.: Dynamic pattern evolution on scale-free networks. PNAS **102**, 10052 (2005).
[4] Zhou, H., and Lipowsky, R.: Activity patterns on random scale-free networks: Global dynamics arising from local majority rules. J. Stat. Mech: Theory and Experiment **2007**, 01009 (2007).

Stochastic Modeling in Ecology and Evolution

Angelo Valleriani 14.03.1966
1992: Diploma, Physics (University of Bologna)
Thesis: Conformal Invariance, Renormalization Group and Integrable Models in Two-Dimensional Quantum Field Theories
1996: PhD, High-Energy Physics (SISSA-ISAS, Triest)
Thesis: Form Factors and Correlation Functions
1996-1998: Postdoc (Max Planck Institute for the Physics of Complex Systems, Dresden)
1998-2000: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2000: Group Leader and IMPRS Coordinator (Max Planck Institute of Colloids and Interfaces, Potsdam)

Most environments in which life evolves have a stochastic nature. For a single natural population a particularly important element of stochasticity is produced by variations over time of the resources necessary for growth and reproduction. Another source of variation comes from the emergence of mutations that can spread in the population and change its structure in a stochastic manner. If we consider a group of species organized in a food web, the arrival of a new species (e.g. through immigration) or the local extinction of another species change the topology of the food web in an unpredictable manner.

Evolution of Dormancy

An interesting example of how natural populations cope with variations in time of the resources is provided by organisms leaving in extreme seasonal environments, where the conditions for growth and reproduction vary strongly from season to season. A much studied case of this kind is given by plants in deserts. In this environment, most plants are restricted to live only a few months during winter and the yield, i.e. the number of seeds produced by each plant, can strongly vary from season to season. Sometimes, even zero yields can occur. 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, at the beginning of each of the next seasons the seeds will germinate only with a certain probability $g<1$ even if the conditions for germination are optimal. These seeds are then called dormant. Thus, dormancy is a strategy that maintains a permanent soil seed bank, which allows local populations to avoid extinction after seasons without yield **[1]**.

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: we determine whether a small population playing the strategy g' can invade an environment dominated by a larger population playing the strategy g. By means of both analytical and numerical techniques **[2]**, this method allows to compute the strategy g^* which survives attempts of invasion by any other strategy. The strategy g^* is then called the evolutionarily stable strategy of the system. This means that evolution should lead to the phenotype g^*.

The analysis of how the evolutionarily 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 statistical properties of the yield per season.

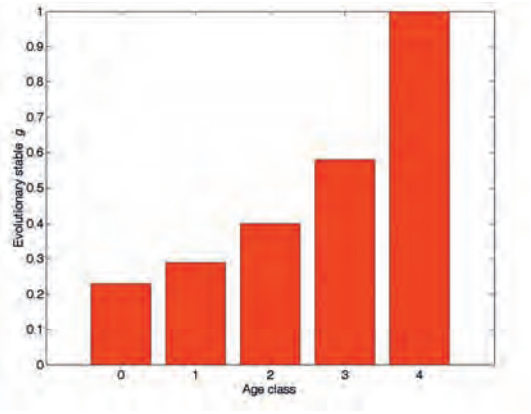


Fig. 1: The evolutionarily stable strategy for structured seed banks is that older seeds (right) have higher germination probability than younger seeds (left).

A particular issue that interested us was the analysis of the evolutionarily stable strategy when the seed bank is structured. One 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 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 but no theory existed to investigate this point. 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 behavior **[3]**.

Another, less obvious seed bank structure became clear from several empirical studies. It was noticed that several plant species in distinct locations produce seeds, which have a low germination probability after a large yield season, and seeds with a large germination probability after a low yield season (**Fig. 2**).

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 **[4]**.

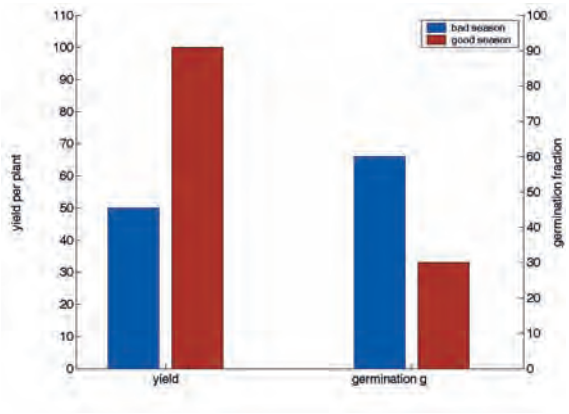


Fig. 2: Seeds from a bad season (blue) have a larger germination probability than seeds from a good season (red).

Given the very general assumptions of the model, we concluded that this behavior should be common to all annual species with permanent soil seed banks.

Often, empirical work aimed at measuring germination behavior is done by collecting and comparing seeds from different geographic locations, which show differences in the year-to-year time correlation of the environmental variables. These correlations, which have been discovered to be very common, are particular important in systems whose adaptive behavior depends on the degree of unpredictability of the quality of a given season. Since the theory so far could not take into account this effect in modeling seed dormancy, I have thus developed a model for the adaptive dynamics of dormancy with which the correlation in the yield are taken into account **[5]**. The result is that positive correlations soften the effect of stochasticity and thus enhance germination, while negative correlation work in the opposite direction.

The Structure of Ecological Networks

For a long time, ecologists are looking for explanations for the amount of biodiversity found in natural systems. It is in fact easy to show why biodiversity should be limited but it proved to be non-trivial to show under which conditions biodiversity can be large. In a sequence of two papers **[6, 7]** we took up this question and compared several mechanistic models using both mean field analysis and computer simulations.

Independently of the details of the mechanistic models, we found a relationship between the ecological characteristics of each species, which we called productivity, and the number of species that can coexist in a food web. Indeed, we have found that the variance of the productivities in a whole food web must decrease at least like 1/S in order to accommodate S species in the network **[6]**. Moreover, by simulating an ecological network in steady state under non equilibrium conditions of immigration and extinction, we could show that biodiversity increases as a power law of the immigration rate, in agreement with the empirical observations **[7]**.

When populations are split into groups connected by a migration network, the fate of mutants willing to spread into the whole population may depend on the structure of the network. By considering the simple Moran process for the population dynamics within each group and within the population, we have shown that a network with a preferred migration direction works against natural selection. This means that the probability of fixation of a favorable mutant is smaller than the probability of fixation in a non-structured or homogeneous network **[8]**.

Angelo Valleriani,
Angelo.Valleriani@mpikg.mpg.de

References:

[1] Bulmer, M.G. "Delayed Germination of Seeds: Cohen's Model Revisited". Theoretical Population Biology **26**, 367-377 (1984).

[2] Valleriani, A.: "Algebraic Determination of the Evolutionary Stable Germination Fraction". Theoretical Population Biology **68**, 197-203 (2005).

[3] Valleriani, A. and Tielbörger, K.: "Effect of Age on Germination of Dormant Seeds", Theoretical Population Biology **70**, 1-9 (2006).

[4] Tielbörger, K. and Valleriani, A.: "Can Seeds predict their Future? Germination Strategies of Density-Regulated Desert Annuals", OIKOS **111**, 235-244 (2005).

[5] Valleriani, A.: "Evolutionarily Stable Germination Strategies with Time-Correlated Yield", Theoretical Population Biology **70**, 255-271 (2006).

[6] Bastolla, U., Lässig, M., Manrubia, S.C. and Valleriani A.: "Biodiversity in Model Ecosystems, I: Coexistence Conditions for Competing Species", J. Theor. Biol. **235**, 521-530 (2005).

[7] Bastolla, U., Lässig, M., Manrubia, S.C. and Valleriani A.: "Biodiversity in Model Ecosystems, II: Species Assembly and Food Web Structure", J. Theor. Biol. **235**, 531-539 (2005).

[8] Valleriani, A. and Meene, T.: "Multilevel Selection in a Gradient", submitted to Ecological Modelling.

Holding with Invisible Light: Optical Trapping of Small and Large Colloidal Particles

Rumiana Dimova 06.04.1971
1995: Diploma, Chemistry (Sofia University, Bulgaria), Major: Chemical Physics and Theoretical Chemistry, Thesis: Role of the Ionic-Correlation and the Hydration Surface Forces in the Stability of Thin Liquid Films
1997: Second MSc (Sofia University, Bulgaria) Thesis: Interactions between Model Membranes and Micron-Sized Particles
1999: PhD, Physical Chemistry (Bordeaux University, France) Thesis: Hydrodynamical Properties of Model Membranes Studied by Means of Optical Trapping Manipulation of Micron-Sized Particles
2000: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2001: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Early works on trapping and levitation of small objects by laser beams date back to the 1970s. Optical tweezers are now a widespread tool based on three-dimensional trapping by a single tightly focused laser beam (**Fig. 1a**). In general, the necessary condition for optical trapping of a particle is that the refractive index of the latter is higher than the one of the surrounding media. Due to the shape of the beam and the refraction from the surface of the particle, the bead is pushed towards the zone with higher intensity, i.e. the beam waist of the laser beam. Thus, using light one can manipulate particles without mechanically touching them. Even though they are difficult to work with because of being invisible for the human eye, infrared laser sources are preferred for the lower potential damage on biological samples.

The simplicity of laser tweezers stems from the fact that to construct a trap one just needs a single collimated beam, directed through a microscope objective with a very large aperture. The latter condition implies using short-working-distance objectives, which restrict optical manipulation to the high magnification end of the microscope nosepiece. Certain applications of optical trapping demand long-working distances at moderate magnification. This can be achieved using a two-beam trapping configuration where two counterpropagating laser beams are used (**Fig. 1b**).

Both single- and two-beam trappings have advantages and drawbacks. All of the limitations of the single-beam trap are consequences of the requirement of a very large aperture objective. (i) Such objectives are of immersion type and have extremely short-working distances: one is limited to working at distances not larger than about 10 μm above the chamber bottom. (ii) They are at the high magnification end (100x is standard) of the microscope nosepiece, providing a relatively narrow field of view. (iii) Large aperture means high resolution, which is profitable, but involves, at the same time, tight focusing and very high power density. The latter often causes heating and optical damage to the sample.

The two-beam geometry represents an opposite tradeoff. Beams are weakly focused by low aperture objectives, allowing for long working distances, low magnification and large field of view, and moderate intensities. Drawbacks are (i) a definitely higher complexity of the optical setup, which needs shaping, aligning, and precisely positioning a couple of counterpropagating beams; and (ii) the trapping geometry depends on the particle size.

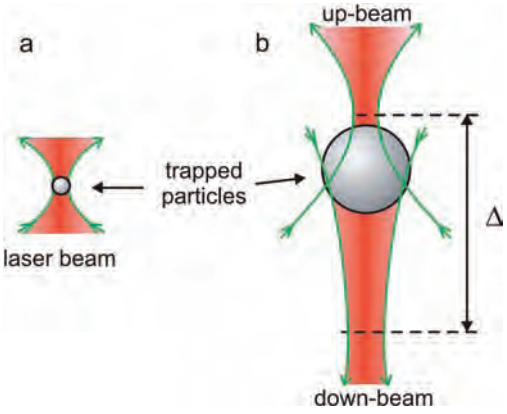


Fig. 1: A schematic illustration of single-beam (a) and double-beam optical trapping (b). In the first case, the laser beam is tightly focused by the objective and the particle is trapped at the beam waist position. In the case of a double-beam trap, two counterpropagating beams are used, up-going and down-going. Their beam waists are located above and below the bead, forming a trapping cage for the particle. The inter-focal distance Δ is set depending on the particle size.

The particle sizes, which one can trap with the two types of traps, also differ. The single-beam tweezers are usually applied to manipulation of particles with diameters between about 0.5 and 5 micrometers. The lower range is set by the limitation from the optical detection of the manipulated particle. Some enhanced detection systems (for example, quadrant photo diodes, which follow the beam deflection from the trapped particles) can reduce this limit. The upper range of particle sizes is set by the diameter of the beam waist, which, in turn is fixed and depends on the objective characteristics. Thus, particles much larger than the beam waist cannot be suitably trapped. With the two-beam trap, one can easily manipulate large particles of tens of microns in size. However, due to the objectives of low magnification, this configuration cannot be applied to particles smaller than about 2 micrometers.

While single-beam tweezers are commercially available, double-beam traps are found only as home-built setups. Being aware of the advantages of having both configurations, recently in our lab, we developed a complete setup, which combines single- and two-beam trapping **[1]**. Both functions were integrated into a commercial microscope (Zeiss Axiovert 200M), and are compatible with all observation modes of the microscope (phase contrast, differential interference contrast, fluorescent microscopy). The system is fed by a continuous wave

Nd:YAG laser with wavelength 1064 nm. We evaluated the performance of the setup in both trapping modes with latex particles, either fluorescent or not, of different sizes, in the 1–20 µm range. In addition, the trapping ability for manipulating oil droplets and polymer capsules (the latter were provided by the Interface department) was also tested; see **Fig. 2**. Both single-beam and double-beam configuration can be used in the case of capsule manipulation. Because the capsules are much larger than the beam waist, in the single-beam configuration the laser beam is focused on a point located at the shell of the capsule where the force is applied. With the double-beam trap, one can capture the complete capsule in the trapping cage.

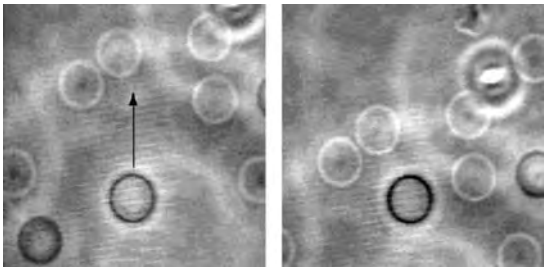


Fig. 2: Demonstration for trapping a polyelectrolyte capsule (phase contrast microscopy). In the setup, the laser beam is immobile and the sample stage is displaced. We trapped a single capsule, levitated it from the bottom of the observation chamber so that the rest of the capsules is out of focus (first snapshot) and displaced the sample stage. In this way, the particle was moved relative to the surrounding solution of capsules (compare with the background in the second snapshot). The direction of the relative displacement is indicated with an arrow in the first snapshot. The capsule diameter is approximately 6 micrometers.

Currently, the setup is used for the manipulation of micron beads with molecular motors attached to them (PhD project of Janina Beeg). The question we attempt to tackle concerns the collective transport of molecular motors. A considerable amount of studies have addressed the transport properties of single motor proteins. But the collective transport performed by several motors, as in the context of transport in cells, has not been studied in detail. As molecular motor we use kinesin, which walks on microtubule tracks. A micron-sized particle with certain kinesin coverage is trapped with the laser tweezers (single-beam mode) and brought to a selected microtubule; see **Fig. 3**. Only a certain fraction of the motors are involved in the bead displacement. The transport properties like walking distance, binding rate and escape force are characterized.

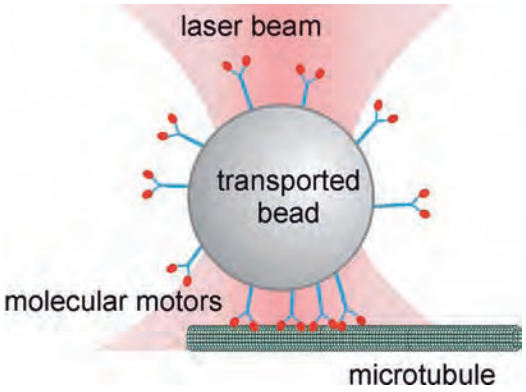


Fig. 3: A schematic illustration of the transport of a bead by several kinesin motors along a microtubule. The particle coverage with motors can be varied depending on the preparation conditions. The bead is trapped by optical tweezers and positioned at a microtubule. If released from the trap, it walks away being pulled by several motors. Switching on the trap again can apply a force in the picoNewton range which is enough to stop the processing bead.

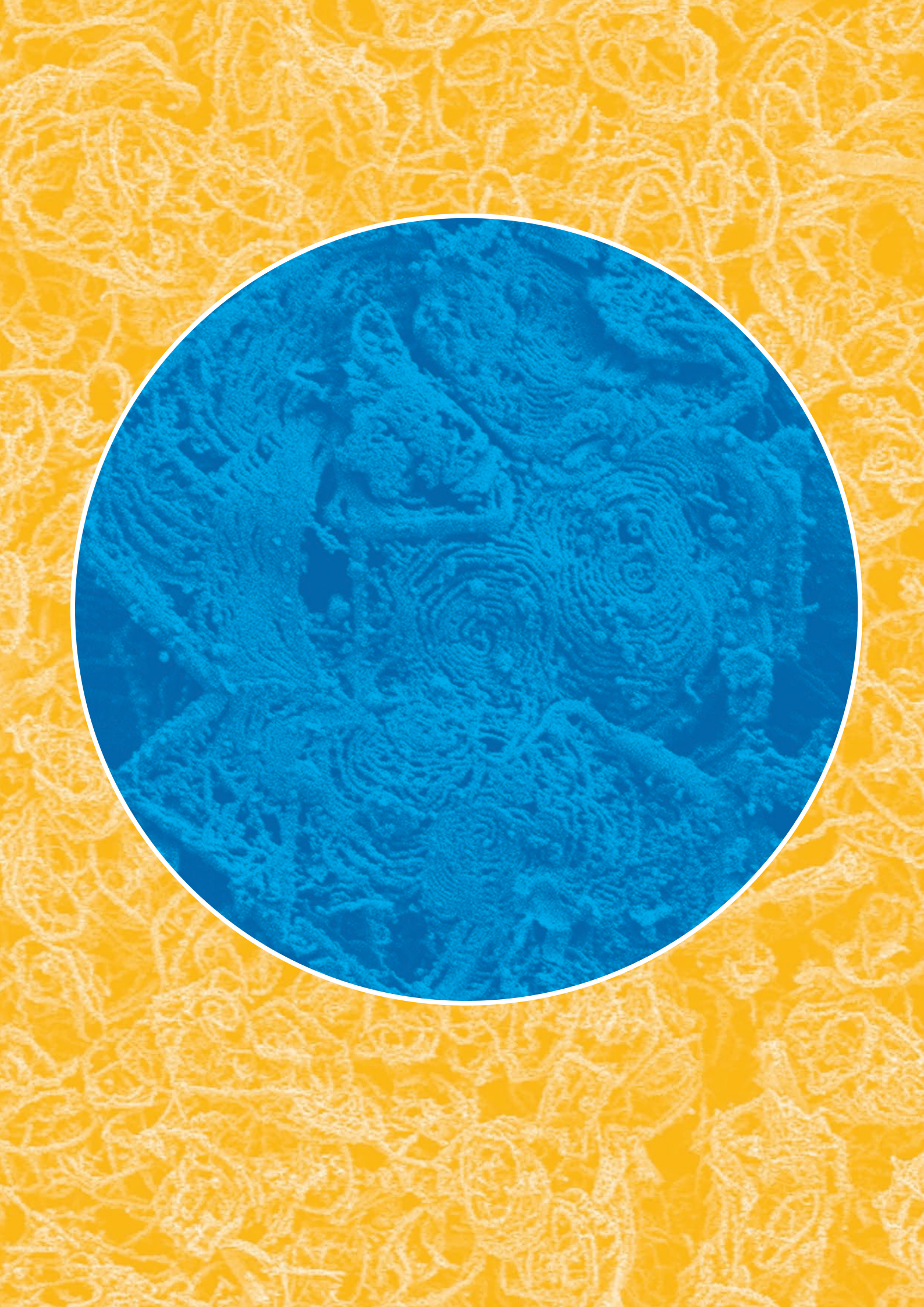
R. Dimova, J. Beeg, P. Kraikivski
Rumiana.Dimova@mpikg.mpg.de

References:

[1] Kraikivski, P., Pouligny, B. and Dimova, R.: Implementing both short- and long-working-distance optical trapping into a commercial microscope, Rev. Sci. Instrum. **77**, 113703 (2006).

[2] Beeg, J., Klumpp, S., Dimova, R., Gracia, R. S., Unger, E. and Lipowsky, R.: Transport of beads by several kinesin motors, submitted.

APPENDIX



Organigramm
Organization Chart

Biomaterials
Director: Prof. Peter Fratzl · Secretary: Kerstin Gabbe

Biological Materials
- Mineralized Tissues/Dr. Himadri S. Gupta
- Bone Regeneration/Dr. Inderchand Manjubala
- Mechanobiology/Dr. Richard Weinkamer
- Plant System Biomechanics/Dr. Ingo Burgert
- Bone Material Quality and Osteoporosis Research/Prof. Peter Fratzl

Biological and Bioinspired Materials
- Biological and Bio-Inspired Materials/Dr. Barbara Aichmayer, Dr. Rivka Elbaum, Dr. Paul Zaslansky, Prof. Peter Fratzl

Bio-Inspired Materials
- Mesoscale Materials and Synchrotron Research/Dr. Oskar Paris

Colloid Chemistry
Director: Prof. Markus Antonietti · Secretary: Annette Pape

Heterophase Polymerization
- Heterophase Polymerizations – Polymer Dispersions/Dr. Klaus Tauer

Self-organizing Polymers
- Biohybrid Polymers/Dr. Helmut Schlaad
- Polymer-Bioconjugates as Macromolecular LEGO®-Bricks/Dr. Hans G. Börner
- Biomimetic Mineralization/Dr. Helmut Cölfen

Mesoporous Materials and Nanoparticles
- Organic Chemistry Meets Inorganic Materials Synthesis/Dr. Markus Niederberger
  Since January 2007 Assistant Professor (Tenure Track) for Multifunctional Materials at the ETH Zürich
- Synthesis and Characterization of Self-assembled Inorganic Materials/Dr. Bernd Smarsly
  From October 2007 Professor (W2) in Physical Chemisty at the University of Gießen
- Mesoporous "Non-Oxidic" Materials/Dr. Arne Thomas
- Hydrothermal Carbon and Modern Separation Materials/Dr. M. Titirici

Modern Techniques of Colloid Analysis
- Fractionating Colloid Analytics/Dr. Helmut Cölfen
- Electron Microscopic Studies of Colloidal Systems and Biomaterials/Dr. Jürgen Hartmann
- Light Scattering at Interfaces/Dr. Reinhard Sigel

Interfaces
Director: Prof. Helmuth Möhwald · Secretary: Karin Kreßler

(Quasi) Planar Interfaces-Fluid Interfaces
- Interactions at Interfaces: Langmuir Monolayers as Model Systems/Dr. Gerald Brezesinski
- Dilational Rheology of Mixed Protein-Surfactant Adsorption Layers/Dr. Reinhard Miller
- Thin Soft Films/Dr. Rumen Krastev
- Ion Distribution at Interfaces/Dr. Hubert Motschmann

Solid Interfaces
- Nucleation, Interfacial Molecular Mobility and Ordering of Alkanes at Solid/Vapor Interfaces/Dr. Hans Riegler

Non-Planar Interfaces
- Nanoscale Membranes: Narrowing the Gap between Materials Science and Biology/Dr. Andreas Fery
  Since March 2006 Professor (W2) in Physical Chemistry at the University Bayreuth
- Multifunctional Polymer Microcapsules/Dr. Gleb Sukhorukhov
  Since March 2005 Chair in Biopolymers at the Queen Mary University of London
- From Molecular Modules to Modular Materials/Dr. Dirk G. Kurth
- Active Coatings Based on Incorporated Nanocontainers/Dr. Dmitry Shchukin
- Bioinspired Control of Electrical and Optical Properties of Interfaces/Prof. Helmuth Möhwald
- Ordering of Functional Nanoparticles/Dr. Dayang Wang

International Joint Laboratories
- Molecular Assembly of Biomimetic Systems and Nanostructures/Prof. Junbai Li

Research Group Nanotechnology for Life Science
- Research Group Nanotechnology for Life Science/Dr. Jean-Francois Lutz

Managing Director (2005-2006)
Prof. Peter Fratzl

Theory & Bio-Systems
Director: Prof. Reinhard Lipowsky · Secretary: Gudrun Conrad

Polymers and Proteins
- Charged Polymers and Polymer Brushes/Dr. Christian Seidel
- Peptide Folding, Peptide Aggregation/Dr. Volker Knecht
- Protein Folding and Folding Kinetics/Dr. Thomas Weikl

Molecular Motors
- Chemomechanical Coupling and Motor Cycles/Prof. Reinhard Lipowsky
- Cooperative Transport and Motor Traffic/Prof. Reinhard Lipowsky

Rods and Filaments
- Semiflexible Rods and Filaments/Dr. Jan Kierfeld
- Phase Behavior of Rigid Rods/Dr. Thomas Gruhn

Membranes and Vesicles
- Membrane Lab/Dr. Rumiana Dimova
- Molecular Dynamics of Membranes/Dr. Volker Knecht
- Mulicomponent Membranes/Dr. Thomas Weikl

Networks in Bio-Systems
- Activity Patterns/Prof. Reinhard Lipowsky
- Network Theories of Evolution/Dr. Angelo Valleriani

Administration/OtherServices
Head: Andreas Stockhaus
Secretary: Rita Heine

Budgeting/Accountancy
Head: Karin Schönfeld
Thea Dumke, Anke Klein, Katharina Zesch

Personnel
Head: Heike Kienert
Ulrike Borchert, Gisela Gutjahr

Procurement/Purchase
Head: Marianne Schulz
Sylvia Ost

Other Services
Head: Andreas Stockhaus
Olaf Gaida, Bodo Ryschka

Location Manager
Reina Schlender

Works Council
Head: Henryk Pitas, Günter Haseloff
Andreas Kretzschmar, Dr. Ingolf Müller,
Olaf Niemeyer, Sylvia Ost,
Christine Pilz, Antje Reinecke,
Dorothea Stscherbina, Thomas Vogt

The Equal Opportunities Commissioners
Antje Reinecke,
Radostina Georgieva

The Ph.D. Students Representatives
Philipp Adelhelm,
Andrea Grafmüller, Petra Gutjahr,
Laura Hartmann, Stefanie Krauß,
Renate Müller, Kerstin Wagner

The Foreign People Commissioner
Georg Garnweitner

IT-Service Group
Heads: Dr. Ingolf Müller,
Roy Pfitzner
Michael Born, Marco Ehlert,
Ingo Fiedler, Hans-Jürgen Schanze

Public Relations
Katja Schulze

Library
Head: Dorothea Stscherbina
Silke Niehaus-Weingärtner

Office for Drawing and Photography
Christine Steininger

Mechanic Workshop
Head: Günter Haseloff
Marco Bott, Andreas Kretzschmar,
Wolfgang Nierenz

Electronic Workshop
Henryk Pitas, Monika Scholz, Wolfgang Stein

Glass Blowing Workshop
Cliff Janiszewski

Campus Technique
Head: Heiko Jung
Hagen Hannemann, Dirk Nast, Heinz Schmidt,
Thomas Vogt

Caretaker
Head: Peter Westermeier

Fachbeirat
Scientific Advisory Board

Name	Institution
Prof. Dr. Colin D. Bain	Department of Chemistry (University of Durham)
Prof. Dr. Kurt Binder	Institut für Physik (Johannes-Gutenberg-Universität Mainz)
Prof. Dr. Ruth Duncan	Welsh School of Pharmacy (Cardiff University)
Prof. Dr. Matthias Drieß	Institut für Chemie (Technische Universität Berlin)
Prof. Dr. Michael Grunze	Physikalisch-Chemisches Institut (Universität Heidelberg)
Prof. Dr. Rüdiger Iden	BASF Aktiengesellschaft
Prof. Dr. George Jeronimidis	School of Construction Management and Engineering (The University of Reading)
Prof. Dr. Michael L. Klein	Department of Chemistry (University of Pennsylvania)
Prof. Dr. Deborah E. Leckband	Department of Chemical & Biomolecular Engineering (The University of Illinois at Urbana Champaign)
Prof. Dr. Michael Schick	Department of Physics (University of Washington)
Prof. Dr. Viola Vogel	Biologisch-Orientierte Materialwissenschaften (Eidgenössische Technische Hochschule Zürich)
Prof. Dr. Steve Weiner	Department of Structural Biology (Weizmann Institute of Science)

Special thanks to Prof. Gerhard D. Findenegg, Prof. Toyoki Kunitake, Prof. Dominique Langevin, Prof. Wolfgang v. Rybinski and Prof. Erich Sackmann for their many years of work in the Scientific Advisory Board.

Drittmittelprojekte
Third Party Funds

Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
BMBF	Polymere Haftvermittler zur Verbesserung der Eigenschaften funktionaler Papiere	Dr. Riegler GF	01.04.2002-31.03.2005	SCA Hygiene Products GmbH, Fraunhofer-Gesellschaft f. Angewandte Forschung e.V., Capsolution Nanoscience AG
BMBF	Nanobiotechnologie-Verbundprojekt: Multifunktionale künstliche Zellen als Transporter, Sensoren und Nanoreaktoren	Prof. Sukhorukov GF	01.05.2002-30.04.2005	Universität Leipzig, Capsulution Nanoscience AG
BMBF	Bionik (2): Übertragung des Konzepts der Matrix-einbettung von Pflanzenfasern auf technische Faserverbundwerkstoffe	Dr. Burgert BM	01.07.2006-31.03.2007	Institut für Textil- und Verfahrenstechnik Denken-dorf, Botanischer Garten der Universität Freiburg
BMWA/AIF	Entwicklung neuartiger Detektions- und Mess-methoden für die Analytik von Kolloiden; Detektorentwicklung und Anwendung für die Analytik von Kolloiden	Prof. Antonietti Dr. Cölfen KC	03.01.2005-31.12.2006	
FWF Wien	Charakterisierung unbehandelter und modifizierter Holzfasern	Dr. Burgert BM	01.11.2003-31.10.2006	
HMI Bln.GmbH	Wissenschaftliche und technische Zusammen-arbeit auf dem Gebiet der Untersuchung von Oberflächen und dünnen Schichten mit Neutronenstreuung	Prof. Möhwald GF	01.01.1999-	
DFG	Mesoskopisch strukturierte Verbundsysteme; Hierarchische Architekturen aus Modulen mit metallosupramolekularen Koordinations-Polyelektrolyten	Prof. Möhwald Dr. Kurth GF	01.01.2001-	
DFG	Mesoskopisch strukturierte Verbundsysteme; Strukturbildung und Dynamik in selbstorgani-sierenden Blockcopolymer-Tensid-Mischsystemen	Dr. Schlaad KC	01.01.2004-	Technische Universität Berlin
DFG	Mesoskopisch strukturierte Verbundsysteme; Ordnungsstrukturen in Systemen aus stäbchen-förmigen Molekülen	Dr. Gruhn Prof. Lipowsky TH	01.01.2004-	
HMI Berlin	Mesoskopisch strukturierte Verbundsysteme; Strukturbildung von Polyelektrolyten und Kolloiden an flüssigen Grenzflächen und in dünnen Filmen	Prof. v. Klitzing GF	01.01.2004-	

BM – Abteilung Biomaterialien/Department of Biomaterials
GF – Abteilung Grenzflächen/Department of Interfaces
KC – Abteilung Kolloidchemie/Department of Colloid Chemistry
TH – Abteilung Theorie & Bio-Systeme/Department of Theory & Bio-Systems

Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Mesoskopisch strukturierte Verbundsysteme; Molekulare Prozesse in mesoskopisch strukturierten Polyelektrolytsystemen	Prof. Möhwald GF	01.01.2004-	Technische Universität Berlin
DFG	Emmy-Noether-Programm: Bioorganische und biomimetische Polymere: Synthese, Charakterisierung und Anwendung der Polymerhybridsysteme – Nachwuchsgruppe	Dr. Börner KC	01.04.2003-31.12.2006	
DFG	Emmy-Noether-Programm: Bioorganische und biomimetische Polymere zur programmierbaren Strukturierung synthetischer Polymermaterialien: Synthese, Charakterisierung und Anwendung der Polymerhybridsysteme	Dr. Börner KC	01.04.2005-	
DFG	Emmy-Noether-Programm: Modelling forces and signalling in cell adhesion – Nachwuchsgruppe	Dr. Schwarz TH	01.01.2004-31.01.2005	
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	Higher Levels of Self-Assembly of Ionic Amphiphilic Colpolymers (SONS-AMPHI)	Dr. Schlaad KC	01.10.2003-	
DFG	Synthese von Nanodrähten und Nanoröhren durch kontrollierte Organisation oberflächenfunktionalisierter Metalloxid-Nanopartikel	Dr. Niederberger KC	15.07.2004-14.04.2007	
DFG	Spektroskopische ellipsometrische Lichtstreuung an Flüssigkristall-Miniemulsionen	Dr. Sigel KC	01.01.2005-31.08.2007	
DFG	Kombination von Reflektions-Interferenz-Kontrast Mikroskopie mit kraftmikroskopischen Methoden zur Untersuchung von Adhäsion und mechanischen Eigenschaften von Polyelektrolyt-Hohlkörpern	Dr. Fery GF	01.05.2006-	
DFG	Retrosynthese von Biomineralien über mesoskopische Transformation von amorphen Precursopartikeln in natürlichen organischen Matrizen	Dr. Cölfen KC	01.01.2006-	
DFG	Structure Elucidation of shear oriented ionic self-assembled materials (SISAM)	Prof. Antonietti KC	09.09.2003-	
DFG	Adhäsion und Fusion von Lipid-Membranen	Dr. Dimova, Prof. Lipowsky TH	01.01.2004-	
DFG	Amyloidprotein-Lipid-Wechselwirkung an Grenzflächen	Dr. Brezesinski GF	01.03.2003-28.02.2005	

Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Untersuchung der spezifischen Wechselwirkung maßgeschneiderter Blockcopolymere und Polypeptide mit Mineraloberflächen in AFM-Desorptionsmessungen	Dr. Cölfen KC	01.11.2003-31.12.2005	
DFG	Kristallisation von Calciumcarbotnat und -phosphat über mesoskopische Transformation von Precursorpartikeln in natürlichen organischen Matrizen als Template und Modellsysteme für Biomaterialien	Dr. Cölfen KC	15.10.2003-31.12.2005	
DFG	Entwicklung von katalytisch aktiven Dendrizymen mit enzymanalogem Struktur-Wirkungsprofil	Dr. Kurth GF	15.07.2004-14.06.2006	
DFG	Counterion Distribution in aligned Lamellar Phases and on Monolayers at the air/water Interface	Prof. Möhwald GF	01.11.2004-	
DFG	Controlled Precipitation of Biominerals using Catanionic Surfactant Self-Assembly Structures	Dr. Cölfen KC	15.08.2004-	
DFG	Complex fluids: From 3 to 2 Dimensions (Deutsch-Französisches Netzwerk)	Prof. Möhwald GF	01.01.2003-	
DFG	Adsorptionsdynamik von Tensiden an Grenzflächen zwischen zwei Flüssigkeiten in Anwesenheit von Lösungsmittelgradienten	Dr. Miller GF	01.10.2004-30.09.2006	
DFG	Molecular magnetism of metallo-supromolecular, hierarchically ordered materials containing periodically arranged metal-ligand-complexes	Dr. Kurth GF	01.06.2005-	
DFG	Controlled Radical Polymerization (CRP) in aqueous heterophase systems	Dr. Tauer KC	01.11.2004-04.09.2005	
DFG	Structure-mechanical property relations of polyelectrolyte multilayer and free-standing membranes	Dr. Fery GF	01.05.2006-	
DFG	Finanzierung von Gastaufenthalten ost- und mitteleuropäischer Wissenschaftler	Dr. Vollhardt GF	01.03.2006-31.05.2006	
DFG	Remote (microwave) activated release from composite nanoparticle/polymer microcapsules (Deutsch-Russisches Kooperationsprojekt)	Prof. Möhwald GF	17.10.2006-	
DFG/RFBR	Remote (microwave) activated release from composite nanoparticle/polymer microcapsules	Prof.Sukhorukov, Dr. Shchukin GF	09.2006-2008	Institute of Regio-engineering and Electronics (RAN) Moscow
DAAD	Projektbezogener Austausch mit Portugal	Dr. Brezesinski GF	01.01.2006-31.12.2007	
DAAD	Projektbezogener Austausch mit Griechenland	Dr. Sigel KC	01.01.2006-31.12.2007	
DAAD	Projektbezogener Austausch mit Bulgarien	Dr. Miller GF	01.01.2005-31.12.2006	

EU

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
ESA	Bone Structure, Changes in Microgravity	Dr. Saparin BM	01.10.2004-30.09.2005	Charité, Berlin Unversität Potsdam ZIB Berlin University of Aarhus Scaco Medical AG Siemens AG Indeed Visual Concepts GmbH
ESA/ESTEC	FASES - Fundamental and applied studies of emulsion stability	Dr. Miller GF	01.10.2003-31.12.2008	IENI, Genua, Italien Université Aix-Marseille Université Compiegne, France Universität Complutense Madrid Universität Florenz IPF, Dresden Aristotele Universität Thessaloniki
ESA/ESTEC	Topical Team: Foam and Emulsion Technologies-Concerted Action Team	Dr. Miller GF	01.10.2003-30.09.2007	CNR, Genua, Italien Universität Lorence, Italien Universität Marseille, Frankreich Universität Compienge, Frankreich IPF Dresden
EU	Self-organized nanostructures of amphiphilic copolymers	Prof. Antonietti KC	01.01.2004-31.12.2007	Technische Universität Berlin Wageningen Universiteit, Niederlande Commissariat a l´energie atomique, Paris Centre National de la Recherche Scientifique, Paris Univerzita Karlova v Praze, Prag BASF AG, Ludwigshafen Rhodia Recherches S.A., Frankreich Universität Basel, Schweiz Moscow State University, Russland
EU	Nanocapsules for Targeted Controlled Delivery of Chemicals	Prof. Sukhorukov Prof. Möhwald GF	01.03.2004-28.02.2007	SINTEF, Norwegen UFC, Frankreich ICSC, Poland CERTH/CPERI , Griechenland PlasmaChem, Mainz Coventya, Frankreich IFP, Frankreich KeraNor, Norwegen Coatex, Frankreich ICB, Polen

EU

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
EU	Early Stage Research Training on Biomimetic Systems	Prof. Lipowsky Dr. Valleriani TH	01.09.2004-31.08.2008	University of Copenhagen Politecnico di Milano Universite Paul Sabatier Toulouse University of Edinburgh University of Leoben
EU	Self-Organisation under Confinement	Dr. von Klitzing GF	01.01.2005-31.12.2008	Kungliga tekniska Högskolan, Stockholm Sofijski Universitet Kliment Ohridski, Sofia Universitas Vilnensis, Vilnius University of Oxford Akzo Nobel Surface Chemistry AB, Schweden Eoetvoes Lorand University, Budapest Aarhus Universitet, Dänemark Universite de Paris, Frankreich Lunds Universitet, Schweden
EU	Nanoengineered chemical Synthesis Inside Restricted Volume of Nano- and Microsized Polyelectrolyte Capsules	Prof. Möhwald Prof. Sukhorukov GF	01.05.05-30.04.07	
EU	Active Biomemetic Systems	Prof. Lipowsky Dr. Valleriani TH	01.05.2005-30.04.2008	Stiching voor Fundamenteel Onderzoek der Materie, Niederlande BASF AG, Deutschland Institute Curie Section Recherche, Frankreich European Molecular Biology Laboratory, Deutschland Institut für Molekulare Biotechnologie, Deutschland Centre National de la Recherche Scientifique, Frankreich Politecnico di Milano, Italien Universität Leipzig, Deutschland
EU	Development of Multifunctional Nanometallic Particles using a new ProcessSonoelectrochemistry	Prof. Möhwald, Prof. Sukhorukov GF	01.03.2005-28.02.2008	Universität Padua, Italien Coventry University, UK University of Kent, UK Hebrew University of Jerusalem, Israel POMETON S.p.A., Italien INKSURE Ltd., Israel BASF AG, Deutschland O.S.M.-DAN Ltd., Israel

EU

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
EU	Open ToK: On Process and Engineering of Nanoporous Materials	Prof. Möhwald Dr. Fery GF	01.03.2006-28.02.2010	Universität Tarragona, Spanien Univerisité Henri Poincaré, Nancy University of Liverpool, UK Academy of Sciences of Czech Republic Virginia Commonwealth University, USA Centre National de la Recherche Scientifique, Frankreich
EU	System for in-situ theranostic using micro-particles triggered by ultrasound	Dr. Fery GF	01.10.2006-30.09.2009	Consorzio Roma Ricerche, Rom Universita degli Studi die Roma, Italien Kungliga tekniska Högskolan, Stockholm University of Ireland, Dublin Karolinska Institute, Stockholm Instituto Nazionale per lo studio e la cura die Tumori, Mailand Medtronic bakken Reserach Center B. V., Niederlande Capsulution NanoScience AG EBIT AET S.P.A., Italien
EU	Novel Materials for Silicate-Based Fuel Cells	Prof. Möhwald Dr. Shchukin GF	01.12.2006-30.11.2009	University of Averio, Portugal Foundation of Research and Technology Hellas, Griechenland Katholieke Universiteit Leuven, Belgien Boreskov Institute of Catalysis, Russland Ceramics and Refractories Technological Development Company, Griechenland Technische Universität Clausthal Ceramics Techniques et Industrielles, Frankreich

Stiftungen

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
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 Berlim
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
A.v.H.	Sofia Kovalevskaja- Preis	Prof.Sukhorukov GF	01.12.2001-31.12.2005	
NCSU	Single-Step Portein Surface-Attachment to Electrospun Fibers	Dr. Börner KC	01.05.2004-30.04.2007	
GIF	Understanding the Toughness of Biological Mineralised Tissues	Prof. Fratzl BM	01.01.2005-31.12.2007	Weizmann Institute of Science, Rehovot
LIKAT	Unterauftrag zum AIF-Projekt: Mesoporöse Hybridsysteme	Prof. Antonietti Dr. Smarsly KC	01.09.2006-31.08.2008	Leibniz-Institut für Katalyse, Rostock
Forsyth Institute	Forsyth Institute	Prof. Fratzl BM	01.08.2005-31.07.2007	
Human Frontier Science Program (HFSP)	Theoretical Modelling of Actin Polymerization	Prof. Lipowsky TH	01.04.04-31.03.07	

Industrie

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
Degussa	Entwicklung, Herstellung und Charakterisierung von mittels Miniemulsionspolymerisation verkapselten Pigmenten	Prof. Antonietti KC	01.01.2004-01.01.2006	
Merck	Improvement and development of new monolithic sol-gel materials/Investigation of model systems for thin films of hierachical meso-structured pore systems and transfer to open tubular campilar systems for nano-LC	Prof. Antonietti Dr. Smarsly KC	01.03.2004-31.10.2008	
Clariant	Steuerung von Kristallisationsprozessen bei Pigmenten durch polymere Additive	Prof. Antonietti Dr. Cölfen KC	01.10.2004-30.09.2006	
BASF	Mesoporöse Hybridsysteme	Prof. Antonietti Dr. Smarsly KC	01.05.2006-30.04.2007	
Servier	Bone Material characteristic after 3 years of strontium ranelate treatment	Prof. Fratzl BM	01.09.2006-30.08.2009	I.R.I.S., Frankreich
Henkel	Funktionale Biohybridpolymersysteme	Dr. Börner KC	01.12.2006-30.11.2007	

Ausgewählte Veranstaltungen
Selected Events

- **12. Januar 2005 Poster Session**
- **27. April 2005 Girl's Day**
- **22.-26. May 2005 Wilhelm und Else Heraeus-Seminar 347: Dynamics of Cell and Tissue Structure**
  Physikzentrum Bad Honneff
- **27. May 2005 Alumni Meeting and Poster Session**
  Trends in Colloids and Interface Science
- **11.-16. Juni 2005 Wissenschaftsmarkt im Potsdamer Lustgarten**
  im Rahmen des Wissenschaftssommers 2005 vom 11.-25. June
- **16. August 2005 "A Workbench for Single Macromolecules"**
  Prof. Jürgen Rabe (Humboldt-Universität zu Berlin)
- **27. August 2005 Open Day/Tag der Offenen Türen**
  Research Campus Golm
- **30. November-2. Dezember 2005 Meeting of the Scientific Committee/Fachbeirat and Poster Session**
- **2.-6. July 2006 6th European Conference on Foams, Emulsions and Applications (EUFOAM 2006)**
- **27. April 2006 Girl's Day**
- **10. June 2006 Open Day/Tag der Offenen Türen**
  University Potsdam
- **16. June 2006 Alumni Meeting and Poster Session**
  Trends in Colloids and Interface Science
- **26. June-29. June 2006 Marie-Curie EST Conference "Bio-Systems" Berlin 2006**
  Organized by: Marie-Curie EST on Biomimetic Systems
- **25. September-6. October 2006 Bio-Systems Summer School, Beijing 2006**
  Max Planck Institute of Colloids and Interfaces & Institute of Theoretical Physics of the Chinese Academy of Sciences
- **6. December 2006 From Diffraction to Imaging: International Symposium on Scanning Microbeam Small- and Wide-Angle Scattering of Hierarchically Structured Materials**
  BESSY Adlershof

Wissenschaftliche Abschlüsse
Scientific Degrees

Diploma Theses

Department of Colloid Chemistry:

Barth, A.: Synthese und Strukturänderung von Chromophoren auf der Basis von Retinal. Technische Universität Chemitz (2005).

Hahn, H.: Rezeptorvermittelte Blockcopolymersynthese. Universität Potsdam (2006).

Hentschel, J.: Synthese und Charakterisierung von schaltbaren Peptid-Polymerkonjugaten zur peptidgelenkten Organisation synthetischer Polymere. Universität Potsdam (2006).

Oertel; A.: Abtrennung und Aufkonzentration von polymerstabliliserten Nanopartikeln. Universität Potsdam (2006).

Department of Interfaces:

Dönch, I.: Rasterkraftmikroskopie und Polyelektrolyt Multilagen. Freie Universität Berlin (2005).

Leinweber, C.: Droplet formation in microstructured porous polymeric materials. Universität Potsdam (2005).

Reinhold, B.: In-situ Untersuchungen zur Abscheidung kolloidaler Schichten auf vorstrukturierten Substraten. Universität Potsdam (2006).

Sievers, T.: Multischichten ausvernetzten Koordinationspolyelektrolyten. Berlin (2005).

Master Theses

Department of Interfaces:

Nazaran, P.: Mobility of polyelectrolyte multilayer: Influence of external stimuli. Freie Universität Berlin, Humboldt Universität zu Berlin, Technische Universität Berlin, Universität Potsdam (2005).

Department of Biomaterials:

Kanawka, K. Ultrastructural Deformation in the Fibrillar Matrix of Demineralised Bone, AGH University of Science and Technology Krakow (2006).

PhD Theses

Hartmann, M.: ***Department of Biomaterials:***
Lattice Models in Material Science Diffusion, Trabecular Bone Remodelling and Linear Elastic Networks. Humboldt Universität zu Berlin (2006).

Wagermaier, W.:
Synchrotron X-ray diffraction studies of bone structure and deformation. Montanuniversität Leoben (2006).

Zickler, G.:
Structure and Mechanical Properties of Carbon- and Silica-based Nanomaterials. Montanuniversität Leoben, September (2006).

Ali, A. Md. I.: ***Department of Colloid Chemistry:***
Morphology Control in Nanoscopic Composite Polymer Particles. Universität Potsdam (2005).

Brezesinski, T.:
Herstellung und Charakterisierung Fuktioneller Mesostrukturierter Metalloxidfilme. Universität Potsdam (2005).

Eckhardt, D.:
Rationales Design von Oligopeptid-Organisatoren zur Bildung von nanostrukturierten Polyethylenoxid-Fasern. Universität Potsdam (2005).

Garnweitner, G.:
Nonaqueous Synthesis of Transition Metal Oxide Nanoparticles and Their Formation Mechanism. Universität Potsdam (2005).

Groenewolt, M.:
Nanostrukturierte Materialien durch Neue Templatsysteme und Nutzung Mesoporöser Silikate als Nano-Reaktoren. Universität Potsdam (2005).

Holtze, C.:
Neue Einflüsse und Anwendungen von Mikrowellenstrahlung auf Miniemulsionen und ihre Kompositpolymere. Universität Potsdam (2005).

Justynska, J.:
Towards a Library of Functional Block Copolymers – Synthesis and Colloidal Properties. Universität Potsdam (2005).

Kozempel, S.:
Emulgatorfreie Emulsionspolymerisation – Monomerlösungszustand und Teilchenbildung. Universität Potsdam (2005).

Nozari, S.:
Towards Understanding RAFT Aqueous Heterophase Polymerization. Universität Potsdam (2005).

Polleux, J.:
Ligand-Mediated Synthesis and Assembly of Crystalline Metal Oxide Nanoparticles. Universität Potsdam (2005).

Voß, R.:
Mesoporous organosilica materials with aminefunctions: surface characteristics and chirality. Universität Potsdam (2005).

Ba, J.:
Nonaqueous Synthesis of Metal Oxide Nanoparticles and Their Assembly into Mesoporous Materials. Universität Potsdam (2006).

Bhattacharyya, S. K.:
Detector Development for Analytical Ultracentrifuge. Universität Potsdam (2006).

Franke, D.:
Novel Surfactants for the Production of Functional Nanostructured Materials via the Ionic Self Assembly (ISA) Route. Universität Potsdam (2006).

Gehrke, N.:
Retrosynthese von Perlmutt. Universität Potsdam (2006).

Meyer, M.:
PIPOX-PEP: Kontrollierte Synthese und Aggregationsverhalten von Blockcopolymeren mit schaltbarer Hydrophilie. Universität Potsdam (2006).

Rettig, H.:
Methoden zur Synthese von definierten bioorganisch-synthetischen Blockcoplymeren. Universität Potsdam (2006).

Duan, H.: ***Department of Interfaces:***
Functional Nanoparticles as Self-Assembling Building Blocks and Synthesic Templates. Universität Potsdam (2005).

Elsner, N.:
Nanomechanik und Adhäsion von Polyelektrolytmultischicht-Hohlkapseln. Universität Potsdam (2005).

Kölsch, P.:
Static and dynamic properties of soluble surfactants to the air/water interface. Universität Potsdam (2005).

Kubowicz, S.:
Design and Characterization of Multicompartment Micelles in Aqueous Solution. Universität Potsdam (2005).

Lazar, P.:
Transport mechanisms and wetting dynamics in molecularly thin films of long-chain alkanes at solid/vapour interface: relation to the solid-liquid phase transition. Universität Potsdam (2005).

Maltseva, E.:
Model membrane interactions with ions and peptides at the air/water interface". Universität Potsdam (2005).

Mishra, N C.:
Interactions in and Stability of Thin Liquid Films. Universität Potsdam (2005).

Pinto da Rocha, S. C.:
Interface Controlled Secondary Changes of the Fibril Forming Peptides B18 and Amyloid. Universidade do Porto (2005).

Sieverling, N.:
Kationische Copolymere für den rezeptvermittelten Gentransfer. Universität Potsdam (2005).

Andersen, A.:
Surfactants Dynamics at Interfaces – A series of Second Harmonic Generation experiments. Universität Potsdam (2006).

Delajon, C. B.:
Wechselwirkung von Lipidmembranen mit Polyelektrolytmultischichten. Universität Potsdam (2006).

Gromelski, S.:
Wechselwirkungen zwischen Lipiden und DNA – Auf dem Weg zum künstlichen Virus. Universität Potsdam (2006).

Köhler, R.:
Phasen- und Transportverhalten von Triacontansubmonolagen an der Grenzfläche zwischen Luft und Siliziumoxid/Silizium. Universität Potsdam (2006).

Nolte, M.:
Integration of freestanding polyelectrolyte multilayer membranes in large scale structures. Universität Potsdam (2006).

Prevot, M. E.:
Introduction of a Thermo-sensitive Non-polar Species into Polyelectrolyte Multilayer Capsules for Drug Delivery. Universität Potsdam (2006).

Sczech, R.: Haftvermittlung von Polyelektrolyten zwischen Celluloseoberflächen. Universität Potsdam (2006).

Symietz, C.: Kopplung von Polyelektrolyten und geladenen Lipid-Monoschichten an der Wasser/Luft-Grenzfläche. Universität Potsdam (2006).

Department of Theory and Bio-Systems:

Asfaw Taye, M.: Adhesion of multi-component membranes and strings. Universität Potsdam (2005).

Boroudjerdi, H.: Charged polymer-macroion complexes. Universität Potsdam (2005).

Erdmann, T.: Stochastic dynamics of adhesion clusters under force. Universität Potsdam (2005).

Haluska, C.: Interactions of funktionalized vesicles in the presence of europium (III) chloride. Universität Potsdam (2005).

Kraikivski, P.: Non-equilibrium dynamics of absorbed polymers and filaments. Universität Potsdam (2005).

Kumar N., A.: Molecular dynamics simulations of polyelectrolyte brushes. Universität Potsdam (2006).

Linke, G. T.: Eigenschaften fluider Vesikeln bei endlichen Temperaturen. Universität Potsdam (2005).

Habilitations

Department of Interfaces:

Fery, A.: Micro-Mechanics and Adhesion of Artificial Capsules from Method-development to Understanding Structure-property Relations. Universität Potsdam (2006).

Department of Theory and Bio-Systems:

Kierfeld, J.: Strings and filaments: from vortices to biopolymers. Universität Potsdam (2006).

Personalien
Appointments and Honors

2005

Ehrungen/Mitgliedschaften/Honorarprofessuren
Honors/Memberships/Honorary Professorships

Professor Dr. Dr. h. c. Markus Antonietti — Director of the Colloid Chemistry Department, was appointed as Turner Alfrey Visiting Professor by the Michigan Molecular Institute (MMI).

Dr. Helmut Schlaad — Group Leader in the Department of Colloid Chemistry obtained the Hermann-Schnell Award of the GDCh for the best Junior Faculty Work in Polymer Science.

Dr. Torsten Brezesinski — PhD Student at the Department of Colloid Chemistry obtained the Dieter-Rampacher Award. The Award is annually awarded to the youngest Ph.D. student of the Max Planck Society.

2006

Ruf an eine Universität
Appointments

Dr. Andreas Fery — Group Leader in the Department of Interfaces, accepted a position as Professor (W2) in Physical Chemistry at the University Bayreuth.

Dr. Markus Niederberger — Group Leader in the Department of Colloid Chemistry accepted a position as Assistant Professor (Tenure Track) for Multifunctional Materials at the ETH Zürich.

Ehrungen/Mitgliedschaften/Honorarprofessuren
Honors/Memberships/Honorary Professorships

Professor Dr. Dr. h. c. Markus Antonietti — Director of the Department of Colloid Chemistry, was appointed as Honorary Professor at the University of Science & Technology of China.

Prof. Dr. Reinhard Lipowsky — Director of the Department of Theory & Bio-Systems, was appointed as Honorary Professor at the Humboldt University Berlin.

Prof. Dr. Helmuth Möhwald — Director of the Department of Interfaces, was appointed as Honorary Professor at the Chinese Academy of Sciences.

Dr. Bernd Smarsly — Group Leader in the Department of Colloid Chemistry obtained the Heinz Maier Leibnitz Award 2006.

Dr. Georg Garnweitner — Scientist in the Department of Colloid Chemistry obtained the Publication Award of the Leibniz Kolleg at the University Potsdam.

2007

Ruf an eine Universität
Appointments

Dr. Bernd Smarsly — Group Leader in the Department of Colloid Chemistry accepted a position as Professor (W2) in Physical Chemistry at the University Gießen.

Ehrungen/Mitgliedschaften/Honorarprofessuren
Honors/Memberships/Honorary Professorships

Prof. Dr. Helmuth Möhwald — Director of the Department of Interfaces, obtained the Prix-Gay-Lussac, which is awarded by the French Ministry for Research and Technology in collaboration with the Alexander Humboldt Foundation.

Prof. Peter Fratzl — Director of the Department of Biomaterials, was appointed as Corresponding Member of the Austrian Academy of Sciences.

Wissenschaftliche Veröffentlichungen und Patente
Publications and Patents

Biomaterials 2005

Abasolo, W. P., Yoshida, M., Yamamo, H. and Okuyama, T.: Influence of structure and chemical composition on thermal softening of Palasan canes (Calamus merrillii). Iawa Journal 26, 363-374 (2005).

Aichmayer, B., Margolis, H. C., Sigel, R., Yamakoshi, Y., Simmer, J. P. and Fratzl, P.: The onset of amelogenin nanosphere aggregation studied by small-angle X-ray scattering and dynamic light scattering. Journal of Structural Biology 151, 239-249 (2005).

Aizenberg, J., Weaver, J. C., Thanawala, M. S., Sundar, V. C., Morse, D. E. and Fratzl, P.: Skeleton of Euplectella sp.: Structural hierarchy from the nanoscale to the macroscale. Science 309, 275-278 (2005).

Alemdar, A., Iridag, Y. and Kazanci, M.: Flow behavior of regenerated wool-keratin proteins in different mediums. International Journal of Biological Macromolecules 35, 151-153 (2005).

Burgert, C. and Fratzl, P.: The stick-slip mechanism in wood: evidence for a critical role of hemicelluloses in the mechanical performance. Christchurch New Zealand, 69-75 (2005).

Burgert, I., Eder, M., Frühmann, K., Keckes, J., Fratzl, P. and Stanzl-Tschegg, S.: Properties of chemically and mechanically isolated fibres of spruce (Picea abies L. Karst.). Part 3: Mechanical characterisation. Holzforschung 59, 354-357 (2005).

Burgert, I., Frühmann, K., Keckes, J., Fratzl, P. and Stanzl-Tschegg, S.: Properties of chemically and mechanically isolated fibres of spruce (Picea abies L. Karst.). Part 2: Twisting phenomena. Holzforschung 59, 247-251 (2005).

Burgert, I., Gierlinger, N. and Zimmermann, T.: Properties of chemically and mechanically isolated fibres of spruce (Picea abies L. Karst.). Part 1: Structural and chemical characterisation. Holzforschung 59, 240-246 (2005).

Fratzl, P., Fischer, F. D. and Svoboda, J.: Energy dissipation and stability of propagating surfaces. Phys. Rev. Lett. 95, Art. No. 195702 (2005).

Fratzl, P., Gupta, H. S., Paris, O., Valenta, A., Roschger, P. and Klaushofer, K.: Diffracting stacks of cards: some thoughts about small-angle scattering from bone. Progress in Colloid and Polymer Science 130, 32-38 (2005).

Gierlinger, N., Hansmann, C., Roder, T., Sixta, H., Gindl, W. and Wimmer, R.: Comparison of UV and confocal Raman microscopy to measure the melamine-formaldehyde resin content within cell walls of impregnated spruce wood. Holzforschung 59, 210-213 (2005).

Gourrier, A., Gutierrez, M. C. G. and Riekel, C.: Investigation of the structural deformation mechanisms induced by microindentation in a thermotropic liquid crystalline copolyester using synchrotron x-ray microdiffraction. Macromolecules 38, 3838-3844 (2005).

Grabner, M., Muller, U., Gierlinger, N. and Wimmer, R.: Effects of heartwood extractives on mechanical properties of larch. Iawa Journal 26, 211-220 (2005).

Grabner, M., Wimmer, R., Gierlinger, N., Evans, R. and Downes, G.: Heartwood extractives in larch and effects on X-ray densitometry. Canadian Journal of Forest Research-Revue Canadienne de Recherche Forestiere 35, 2781-2786 (2005).

Gupta, H. S., Schratter, S., Tesch, W., Roschger, P., Berzlanovich, A., Schoeberl, T., Klaushofer, K. and Fratzl, P.: Two different correlations between nanoinentation modulus and mineral content in the bone-cartilage interface. Journal of Structural Biology 149, 138-148 (2005).

Gupta, H. S., Wagermaier, W., Zickler, G. A., Aroush, D. R. B., Funari, S. S., Roschger, P., Wagner, H. D. and Fratzl, P.: Nanoscale deformation mechanisms in bone. Nano Letters 5, 2108-2111 (2005).

Hartmann, M. A., Weinkamer, R., Fratzl, P., Svoboda, J. and Fischer, F. D.: Onsager's coefficients and diffusion laws - a Monte Carlo study. Philosophical Magazine 85, 1243-1260 (2005).

Keckes, J., Burgert, I., Müller, M., Kölln, K., Hamilton, M., Burghammer, M., Roth, S. V., Stanzl-Tschegg, S. and Fratzl, P.: In-situ WAXS studies of structural changes in wood foils and in individual wood cells during microtensile tests. Fibre Diffraction Review 13, 48-51 (2005).

Loidl, D., Paris, O., Burghammer, M., Riekel, C. and Peterlik, H.: Direct observation of nanocrystallite buckling in carbon fibers under bending load. Phys. Rev. Lett. 95, Art. No. 225501 (2005).

Loidl, D., Peterlik, H., Paris, O., Muller, M., Burghammer, M. and Riekel, C.: Structure and mechanical properties of carbon fibres: a review of recent microbeam diffraction studies with synchrotron radiation. Journal of Synchrotron Radiation 12, 758-764 (2005).

Maier, G. A., Wallner, G., Lang, R. W. and Fratzl, P.: Structural changes during plastic deformation at crack tips in PVDF films: A scanning X-ray scattering study. Macromolecules 38, 6099-6105 (2005).

Manjubala, I., Sastry, T. P. and Kumar, R. V. S.: Bone in-growth induced by biphasic calcium phosphate ceramic in femoral defect of dogs. Journal of Biomaterials Applications 19, 341-360 (2005).

Manjubala, I., Woesz, A., Pilz, C., Rumpler, M., Fratzl-Zelman, N., Roschger, P., Stampfl, J. and Fratzl, P.: Biomimetic mineral-organic composite scaffolds with controlled internal architecture. Journal of Materials Science-Materials in Medicine 16, 1111-1119 (2005).

Misof, B. M., Roschger, P., Baldini, T., Raggio, C. L., Zraick, V., Root, L., Boskey, A. L., Klaushofer, K., Fratzl, P. and Carnacho, N. P.: Differential effects of alendronate treatment on bone from growing osteogenesis imperfecta and wild-type mouse. Bone 36, 150-158 (2005).

Mueller, R., Köhler, K., Weinkamer, R., Sukhorukov, G. and Fery, A.: Melting of PDADMAC/PSS capsules investigated with AFM force spectroscopy. Macromolecules 38, 9766-9771 (2005).

Paris, O., Zollfrank, C. and Zickler, G. A.: Decomposition and carbonisation of wood biopolymers - a microstructural study of softwood pyrolysis. Carbon 43, 53-66 (2005).

Rusu, V. M., Ng, C. H., Wilke, M., Tiersch, B., Fratzl, P. and Peter, M. G.: Size-controlled hydroxyapatite nanoparticles as self-organized organic-in organic composite materials. Biomaterials 26, 5414-5426 (2005).

Saparin, P. I., Thomsen, J. S., Prohaska, S., Zaikin, A., Kurths, J., Hege, H. C. and Gowin, W.: Quantification of spatial structure of human proximal tibial bone biopsies using 3D measures of complexity. Acta Astronautica 56, 820-830 (2005).

Stewart, T. L., Roschger, P., Misof, B. M., Mann, V., Fratzl, P., Klaushofer, K., Aspden, R. and Ralston, S. H.: Association of COLIA1 Sp1 alleles with defective bone nodule formation in vitro and abnormal bone mineralization in vivo. Calcif. Tissue Int. 77, 113-118 (2005).

Thomsen, J. S., Morukov, B. V., Vico, L., Alexandre, C., Saparin, P. I. and Gowin, W.: Cancellous bone structure of iliac crest biopsies following 370 days of head-down bed rest. Aviation Space and Environmental Medicine 76, 915-922 (2005).

Valenta, A., Roschger, P., Fratzl-Zelman, N., Kostenuik, P. J., Dunstan, C. R., Fratzl, P. and Klaushofer, K.: Combined treatment with PTH (1-34) and OPG increases bone volume and uniformity of mineralization in aged ovariectomnized rats. Bone 37, 87-95 (2005).

Weber, M., Schoeberl, T., Roschger, P., Klaushofer, K. and Fratzl, P.: Relating local bone stiffness and calcium content by combined nanoindentation and backscattered electron imaging. Materials Research Society Symposium Proceedings 874, L1.9, 67-72 (2005).

Weinkamer, R., Hartmann, M. A., Brechet, Y. and Fratzl, P.: Architectural changes of trabecular bone caused by the remodeling process. Materials Research Society Symposium Proceedings 874, L5.11, 79-84 (2005).

Woesz, A., Rumpler, A., Stampfl, J., Varga, F., Fratzl-Zelman, N., Roschger, P., Klaushofer, K. and Fratzl, P.: Towards bone replacement materials from calcium phosphates via rapid prototyping and ceramic gelcasting. Materials Science & Engineering C-Biomimetic and Supramolecular Systems 25, 181-186 (2005).

Woesz, A., Rumpler, M., Manjubala, I., Pilz, C., Varga, F., Stampfl, J. and Fratzl, P.: The influence of the thermal treatment of hydroxylapatite scaffolds on the physical properties and the bone cell in growth behaviour. Materials Research Society Symposium Proceedings 874, L7.9.1 (2005).

Biomaterials 2006

Aichmayer, B., Mertig, M., Kirchner, A., Paris, O. and Fratzl, P.: Small-angle scattering of S-layer metallization. Advanced Materials 18, 915-919 (2006).

Burgert, I.: Exploring the micromechanical design of plant cell walls. American Journal of Botany 93, 1391-1401 (2006).

Burgert, I., Keckes, J. and Fratzl, P.: Mechanics of the wood cell wall. In: Characterization of the cellulosic cell wall. (Ed.) D. D. Stokke and L. H. Groom, Blackwell, Oxford 2006, 30-37.

Deshpande, A. S., Burgert, I. and Paris, O.: Hierarchically structured ceramics by high-precision nanoparticte casting of wood. Small 2, 994-998 (2006).

Durchschlag, E., Paschalis, E. P., Zoehrer, R., Roschger, P., Fratzl, P., Recker, R., Phipps, R. and Klaushofer, K.: Bone material properties in trabecular bone from human iliac crest biopsies after 3- and 5-year treatment with risedronate. J. Bone Miner. Res. 21, 1581-1590 (2006).

Elbaum, M.: Polymers in the pore. Science 314, 766-767 (2006).

Gierlinger, N. and Schwanninger, M.: Chemical imaging of poplar wood cell walls by confocal Raman microscopy. Plant Physiol. 140, 1246-1254 (2006).

Gierlinger, N., Schwanninger, M., Reinecke, A. and Burgert, I.: Molecular changes during tensile deformation of single wood fibers followed by Raman microscopy. Biomacromolecules 7, 2077-2081 (2006).

Gourrier, A., Garcia-Gutierrez, M. C. and Riekel, C.: Hardness testing under a different light: combining synchrotron X-ray microdiffraction and indentation techniques for polymer fibres studies. Philosophical Magazine 86, 5753-5767 (2006).

Gupta, H. S., Seto, J., Wagermaier, W., Zaslansky, P., Boesecke, P. and Fratzl, P.: Cooperative deformation of mineral and collagen in bone at the nanoscale. Proc. Natl. Acad. Sci. U. S. A. 103, 17741-17746 (2006).

Gupta, H. S., Stachewicz, U., Wagermaier, W., Roschger, P., Wagner, H. D. and Fratzl, P.: Mechanical modulation at the lamellar level in osteonal bone. J. Mater. Res. 21, 1913-1921 (2006).

Gupta, H. S., Wagermaier, W., Zickler, G. A., Hartmann, J., Funari, S. S., Roschger, P., Wagner, H. D. and Fratzl, P.: Fibrillar level fracture in bone beyond the yield point. International Journal of Fracture 139, 425-436 (2006).

Hartmann, M. A., Weinkamer, R., Zemb, T., Fischer, F. D. and Fratzl, P.: Switching mechanics with chemistry: A model for the bending stiffness of amphiphilic bilayers with interacting headgroups in crystalline order. Phys. Rev. Lett. 97, Art. No. 018106 (2006).

Iridag, Y. and Kazanci, M.: Preparation and characterization of Bombyx mori silk fibroin and wool keratin. J. Appl. Polym. Sci. 100, 4260-4264 (2006).

Kazanci, M., Fratzl, P., Klaushofer, K. and Paschalis, E. P.: Complementary information on in vitro conversion of amorphous (precursor) calcium phosphate to hydroxyapatite from raman microspectroscopy and wide-angle X-ray scattering. Calcif. Tissue Int. 79, 354-359 (2006).

Kazanci, M., Roschger, P., Paschalis, E. P., Klaushofer, K. and Fratzl, P.: Bone osteonal tissues by Raman spectral mapping: Orientation-composition. Journal of Structural Biology 156, 489-496 (2006).

Kienzler, R., Fischer, F. D. and Fratzl, P.: On energy changes due to the formation of a circular hole in an elastic plate. Archive of Applied Mechanics 76, 681-697 (2006).

Köhler, K., Biesheuvel, P. M., Weinkamer, R., Möhwald, H. and Sukhorukov, G. B.: Salt-induced swelling-to-shrinking transition in polyelectrolyte multilayer capsules. Phys. Rev. Lett. 97, Art. No. 188301 (2006).

Paris, O., Aichmayer, B. and Fratzl, P.: Small-angle scattering from spherical particles on randomly oriented interfaces. Zeitschrift für Metallkunde 97, 290-294 (2006).

Peterlik, H. and Fratzl, P.: Small-angle X-ray scattering to characterize nanostructures in inorganic and hybrid materials chemistry. Monatshefte für Chemie 137, 529-543 (2006).

Peterlik, H., Roschger, P., Klaushofer, K. and Fratzl, P.: Orientation dependent fracture toughness of lamellar bone. International Journal of Fracture 139, 395-405 (2006).

Peterlik, H., Roschger, P., Klaushofer, K. and Fratzl, P.: From brittle to ductile fracture of bone. Nature Materials 5, 52-55 (2006).

Pfau, B., Stadler, L. M., Sepiol, B., Weinkamer, R., Kantelhardt, J. W., Zontone, F. and Vogl, G.: Coarsening dynamics in elastically anisotropic alloys. Phys. Rev. B: Condens. Matter 73, Art. No. 180101 (2006).

Saparin, P., Thomsen, J. S., Kurths, J., Beller, G. and Gowin, W.: Segmentation of bone CT images and assessment of bone structure using measures of complexity. Medical Physics 33, 3857-3873 (2006).

Publications/Department of Biomaterials

Schmidt, M., Gierlinger, N., Schade, U., Rogge, T. and Grunze, M.: Polarized infrared microspectroscopy of single spruce fibers: Hydrogen bonding in wood polymers. Biopolymers 83, 546-555 (2006).

Stadler, L. M., Sepiol, B., Pfau, B., Kantelhardt, J. W., Weinkamer, R. and Vogl, G.: Detrended fluctuation analysis in x-ray photon correlation spectroscopy for determining coarsening dynamics in alloys. Physical Review E 74, Art. No. 041107 (2006).

Svoboda, J., Fischer, F. D. and Fratzl, P.: Diffusion and creep in multi-component alloys with non-ideal sources and sinks for vacancies. Acta Materialia 54, 3043-3053 (2006).

Sykacek, E., Gierlinger, N., Wimmer, R. and Schwanninger, M.: Prediction of natural durability of commercial available European and Siberian larch by near-infrared spectroscopy. Holzforschung 60, 643-647 (2006).

Weber, M., Roschger, P., Fratzl-Zelman, N., Schoberl, T., Rauch, F., Glorieux, F. H., Fratzl, P. and Klaushofer, K.: Pamidronate does not adversely affect bone intrinsic material properties in children with osteogenesis imperfecta. Bone 39, 616-622 (2006).

Woesz, A., Weaver, J. C., Kazanci, M., Dauphin, Y., Aizenberg, J., Morse, D. E. and Fratzl, P.: Micromechanical properties of biological silica in skeletons of deep-sea sponges. J. Mater. Res. 21, 2068-2078 (2006).

Zabler, S., Riesemeier, H., Fratzl, P. and Zaslansky, P.: Fresnel-propagated imaging for the study of human tooth dentin by partially coherent x-ray tomography. Optics Express 14, 8584-8597 (2006).

Zaslansky, P., Friesem, A. A. and Weiner, S.: Structure and mechanical properties of the soft zone separating bulk dentin and enamel in crowns of human teeth: Insight into tooth function. Journal of Structural Biology 153, 188-199 (2006).

Zaslansky, P., Shahar, R., Friesem, A. A. and Weiner, S.: Relations between shape, materials properties, and function in biological materials using laser speckle interferometry: In situ tooth deformation. Advanced Functional Materials 16, 1925-1936 (2006).

Zickler, G. A., Jahnert, S., Wagermaier, W., Funari, S. S., Findenegg, G. H. and Paris, O.: Physisorbed films in periodic mesoporous silica studied by in situ synchrotron small-angle diffraction. Phys. Rev. B: Condens. Matter 73, Art. No. 18410 (2006).

Zickler, G. A., Schoberl, T. and Paris, O.: Mechanical properties of pyrolysed wood: a nanoindentation study. Philosophical Magazine 86, 1373-1386 (2006).

Zickler, G. A., Smarsly, B., Gierlinger, N., Peterlik, H. and Paris, O.: A reconsideration of the relationship between the crystallite size L-a of carbons determined by X-ray diffraction and Raman spectroscopy. Carbon 44, 3239-3246 (2006).

Zoeger, N., Roschger, P., Hofstaetter, J. G., Jokubonis, C., Pepponi, G., Falkenberg, G., Fratzl, P., Berzlanovich, A., Osterode, W., Streli, C. and Wobrauschek, P.: Lead accumulation in tidemark of articular cartilage. Osteoarthritis and Cartilage 14, 906-913 (2006).

Zoehrer, R., Roschger, P., Paschalis, E. P., Hofstaetter, J. G., Durchschlag, E., Fratzl, P., Phipps, R. and Klaushofer, K.: Effects of 3-and 5-year treatment with risedronate on bone mineralization density distribution in triple biopsies of the iliac crest in postmenopausal women. J. Bone Miner. Res. 21, 1106-1112 (2006).

Publications/Department of Colloid Chemistry

Colloid Chemistry 2005

Aichmayer, B., Margolis, H. C., Sigel, R., Yamakoshi, Y., Simmer, J. P. and Fratzl, P.: The onset of amelogenin nanosphere aggregation studied by small-angle X-ray scattering and dynamic light scattering. Journal of Structural Biology 151, 239-249 (2005).

Ali, A. M. L., Tauer, K. and Sedlak, M.: Comparing emulsion polymerization of methacrylate-monomers with different hydrophilicity. Polymer 46, 1017-1023 (2005).

Armelao, L., Eisenmenger-Sittner, C., Groenewolt, M., Gross, S., Sada, C., Schubert, U., Eugenio, T. A. and Zattin, A.: Zirconium and hafnium oxoclusters as molecular building blocks for highly dispersed ZrO_2 or HfO_2 nanoparticles in silica thin films. J. Mater. Chem. 15, 1838-1848 (2005).

Ba, J. H., Polleux, J., Antonietti, M. and Niederberger, M.: Non-aqueous synthesis of tin oxide nanocrystals and their assembly into ordered porous mesostructures. Advanced Materials 17, 2509-2512 (2005).

Börner, H. G. and Eckhardt, D.: Formation of polymer nanofibers facilitated by the self-assembly of template pre-organized oligopeptides. Polymer Preprints 46, 744-745 (2005).

Börner, H. G., Rettig, H., ten Cate, M. G. J., Lutz, J. F. and Krause, E.: Macromolecular chimera via controlled radical polymerization techniques. Polymer Preprints 46, 286-287 (2005).

Bradley, M. A., Prescott, S. W., Schoonbrood, H. A. S., Landfester, K. and Grieser, F.: Miniemulsion copolymerization of methyl methacrylate and butyl acrylate by ultrasonic initiation. Macromolecules 38, 6346-6351 (2005).

Brezesinski, T., Antonietti, M., Groenewolt, M., Pinna, N. and Smarsly, B.: The generation of mesostructured crystalline CeO_2, ZrO_2 and CeO_2-ZrO_2 films using evaporation-induced self-assembly. New J. Chem. 29, 237-242 (2005).

Brezesinski, T., Erpen, C., Iimura, K. and Smarsly, B.: Mesostructured crystalline ceria with a bimodal pore system using block copolymers and ionic liquids as rational templates. Chem. Mater. 17, 1683-1690 (2005).

Brezesinski, T., Smarsly, B., Groenewolt, M., Antonietti, M., Grosso, D., Boissiere, C. and Sanchez, C.: The generation of mesoporous CeO_2 with crystalline pore walls using novel block copolymer templates. Stud. Surf. Sci. Catal. 156, 243-248 (2005).

Brezesinski, T., Smarsly, B., Iimura, K., Grosso, D., Boissiere, C., Amenitsch, H., Antonietti, M. and Sanchez, C.: Self-assembly and crystallization Behavior of mesoporous, crystalline HfO_2 thin films: A model system for the generation of mesostructured transition-metal oxides. Small 1, 889-898 (2005).

Chen, S. F., Yu, S. H., Wang, T. X., Jiang, J., Cölfen, H., Hu, B. and Yu, B.: Polymer-directed formation of unusual $CaCO_3$ pancakes with controlled surface structures. Advanced Materials 17, 1461-1465 (2005).

Cölfen, H.: Analytical ultracentrifugation of colloids. In: Analytical ultracentrifugation: techniques and methods. (Ed.) D. J. Scott, S. E. Harding and A. Rowe, J., Royal Society of Chemistry, Cambridge 2005, 501-583.

Cölfen, H. and Antonietti, M.: Mesocrystals: Inorganic superstructures made by highly parallel crystallization and controlled alignment. Angewandte Chemie-International Edition 44, 5576-5591 (2005).

Cölfen, H. and Yu, S. H.: Biomimetic mineralization/synthesis of mesoscale order in hybrid inorganic-organic materials via nanoparticle self-assembly. MRS Bulletin 30, 727-735 (2005).

Deshpande, A. S., Pinna, N., Smarsly, B., Antonietti, M. and Niederberger, M.: Controlled assembly of preformed ceria nanocrystals into highly ordered 3D nanostructures. Small 1, 313-316 (2005).

Deshpande, A. S., Shchukin, D. G., Ustinovich, E., Antonietti, M. and Caruso, R. A.: Titania and mixed titania/aluminum, gallium, or indium oxide spheres: Sol-gel/template synthesis and photocatalytic properties. Advanced Functional Materials 15, 239-245 (2005).

Dourdain, S., Bardeau, J. F., Colas, M., Smarsly, B., Mehdi, A., Ocko, B. M. and Gibaud, A.: Determination by x-ray reflectivity and small angle x-ray scattering of the porous properties of mesoporous silica thin films. Appl. Phys. Lett. 86, Art. No. 113108 (2005).

Eckhardt, D., Groenewolt, M., Krause, E. and Börner, H. G.: Rational design of oligopeptide organizers for the formation of poly(ethylene oxide) nanofibers. Chemical Communications, 2814-2816 (2005).

Franke, D.: Novel surfactants for the production of functional nanostructured materials via the ionic self-assembly (ISA) route. Potsdam 2005.

Franke, D., Egger, C. C., Smarsly, B., Faul, C. F. J. and Tiddy, G. J. T.: Synthesis and phase characterization of a double-tailed pyrrole-containing surfactant: A novel tecton for the production of functional nanostructured materials. Langmuir 21, 2704-2712 (2005).

Garnweitner, G., Antonietti, M. and Niederberger, M.: Nonaqueous synthesis of crystalline anatase nanoparticles in simple ketones and aldehydes as oxygen-supplying agents. Chemical Communications, 397-399 (2005).

Garnweitner, G., Hentschel, J., Antonietti, M. and Niederberger, M.: Nonaqueous synthesis of amorphous powder precursors for nanocrystalline $PbTiO_3$, $Pb(Zr,Ti)O_3$, and $PbZrO_3$. Chem. Mater. 17, 4594-4599 (2005).

Gehrke, N., Cölfen, H., Pinna, N., Antonietti, M. and Nassif, N.: Superstructures of calcium carbonate crystals by oriented attachment. Crystal Growth & Design 5, 1317-1319 (2005).

Gehrke, N., Nassif, N., Pinna, N., Antonietti, M., Gupta, H. S. and Cölfen, H.: Retrosynthesis of nacre via amorphous precursor particles. Chem. Mater. 17, 6514-6516 (2005).

Groenewolt, M. and Antonietti, M.: Synthesis of g-C_3N_4 nanoparticles in mesoporous silica host matrices. Advanced Materials 17, 1789-1792 (2005).

Groenewolt, M., Brezesinski, T., Schlaad, H., Antonietti, M., Groh, P. W. and Ivan, B.: Polyisobutylene-block-poly(ethylene oxide) for robust templating of highly ordered mesoporous materials. Advanced Materials 17, 1158-1162 (2005).

Groschel, L., Haidar, R., Beyer, A., Cölfen, H., Frank, B. and Schomacker, R.: Hydrogenation of propyne in palladium-containing polyacrylic acid membranes and its characterization. Industrial & Engineering Chemistry Research 44, 9064-9070 (2005).

Publications/Department of Colloid Chemistry

Guan, Y., Yu, S. H., Antonietti, M., Bottcher, C. and Faul, C. F. J.: Synthesis of supramolecular polymers by ionic self-assembly of oppositely charged dyes. Chemistry-a European Journal 11, 1305-1311 (2005).

Harding, S. E., Cölfen, H. and Aziz, Z.: The ELLIPS suite of whole-body protein conformation algorithms for microsoft WINDOWS. In: Analytical ultracentrifugation: techniques and methods. (Ed.) D. J. Scott, S. E. Harding and A. Rowe, J., Royal Society of Chemistry, Cambridge 2005, 468-483.

Havecker, M., Pinna, N., Weiss, K., Sack-Kongehl, H., Jentoft, R. E., Wang, D., Swoboda, M., Wild, U., Niederberger, M., Urban, J., Su, D. S. and Schlogl, R.: Synthesis and functional verification of the unsupported active phase of VxOy catalysts for partial oxidation of n-butane. J. Catal. 236, 221-232 (2005).

Holtze, C., Landfester, K. and Antonietti, M.: A novel route to multiphase polymer systems containing nano-droplets: Radical polymerization of vinylic monomers in gelled water-in-oil miniemulsions. Macromolecular Materials and Engineering 290, 1025-1028 (2005).

Justynska, J., Hordyjewicz, Z. and Schlaad, H.: Toward a toolbox of functional block copolymers via free-radical addition of mercaptans. Polymer 46, 12057-12064 (2005).

Kandre, R. M., Kutzner, F., Schlaad, H. and Schlüter, A. D.: Synthesis of high molecular weight amphiphilic polyphenylenes by Suzuki polycondensation. Macromolecular Chemistry and Physics 206, 1610-1618 (2005).

Khopade, A. J., Arulsudar, N., Khopade, S. A. and Hartmann, J.: Ultrathin antibiotic walled microcapsules. Biomacromolecules 6, 229-234 (2005).

Kozempel, S., Tauer, K. and Rother, G.: Aqueous heterophase polymerization of styrene - a study by means of multi-angle laser light scattering. Polymer 46, 1169-1179 (2005).

Kuemmel, M., Grosso, D., Boissiere, U., Smarsly, B., Brezesinski, T., Albouy, P. A., Amenitsch, H. and Sanchez, C.: Thermally stable nanocrystalline gamma-alumina layers with highly ordered 3D mesoporosity. Angewandte Chemie-International Edition 44, 4589-4592 (2005).

Landfester, K., Pawelzik, U. and Antonietti, M.: Polydimethylsiloxane latexes and block copolymers by polymerization and polyaddition in miniemulsion. Polymer 46, 9892-9898 (2005).

Ludwigs, S., Krausch, G., Reiter, G., Losik, M., Antonietti, M. and Schlaad, H.: Structure formation of a polystyrene-block-poly(gamma-benzyl L-glutamate) in thin films. Macromolecules 38, 7532-7535 (2005).

Lutz, J. F., Börner, H. G. and Weichenhan, K.: Combining atom transfer radical polymerization and click chemistry: A versatile method for the preparation of end-functional polymers. Macromolecular Rapid Communications 26, 514-518 (2005).

Lutz, J. F., Börner, H. G. and Weichenhan, K.: Using "click" chemistry for post-reacting well-defined polymer chains prepared by atom transfer radical polymerization. Polymer Preprints 46, 486-487 (2005).

Mastalir, A., Frank, B., Szizybalski, A., Soerijanto, H., Deshpande, A., Niederberger, M., Schomacker, R., Schlögl, R. and Ressler, T.: Steam reforming of methanol over $Cu/ZrO_2/CeO_2$ catalysts: a kinetic study. J. Catal. 230, 464-475 (2005).

Nassif, N., Gehrke, N., Pinna, N., Shirshova, N., Tauer, K., Antonietti, M. and Cölfen, H.: Synthesis of stable aragonite superstructures by a biomimetic crystallization pathway. Angewandte Chemie-International Edition 44, 6004-6009 (2005).

Nassif, N., Pinna, N., Gehrke, N., Antonietti, M., Jager, C. and Cölfen, H.: Amorphous layer around aragonite platelets in nacre. Proc. Natl. Acad. Sci. U. S. A. 102, 12653-12655 (2005).

Neri, G., Bonavita, A., Micali, G., Rizzo, G., Galvagno, S., Niederberger, M. and Pinna, N.: A highly sensitive oxygen sensor operating at room temperature based on platinum-doped In_2O_3 nanocrystals. Chemical Communications, 6032-6034 (2005).

Niederberger, M., Garnweitner, G., Pinna, N. and Neri, G.: Non-aqueous routes to crystalline metal oxide nanoparticles: Formation mechanisms and applications. Progress in Solid State Chemistry 33, 59-70 (2005).

Nozari, S. and Tauer, K.: Calorimetric study on the influence of the nature of the RAFT agent and the initiator in ab initio aqueous heterophase polymerization. Polymer 46, 1033-1043 (2005).

Pinna, N., Garnweitner, G., Antonietti, M. and Niederberger, M.: A general nonaqueous route to binary metal oxide nanocrystals involving a C-C bond cleavage. Journal of the American Chemical Society 127, 5608-5612 (2005).

Pinna, N., Garnweitner, G., Beato, P., Niederberger, M. and Antonietti, M.: Synthesis of yttria-based crystattine and lamellar nanostructures and their formation mechanism. Small 1, 112-121 (2005).

Pinna, N., Grancharov, S., Beato, P., Bonville, P., Antonietti, M. and Niederberger, M.: Magnetite nanocrystals: Nonaqueous synthesis, characterization, and solubility. Chem. Mater. 17, 3044-3049 (2005).

Polleux, J., Pinna, N., Antonietti, M., Hess, C., Wild, U., Schlögl, R. and Niederberger, M.: Ligand functionality as a versatile tool to control the assembly behavior of preformed titania nanocrystals. Chemistry-a European Journal 11, 3541-3551 (2005).

Polleux, J., Pinna, N., Antonietti, M. and Niederberger, M.: Growth and assembly of crystalline tungsten oxide nanostructures assisted by bioligation. Journal of the American Chemical Society 127, 15595-15601 (2005).

Ruland, W. and Smarsly, B.: SAXS of self-assembled nanocomposite films with oriented two-dimensional cylinder arrays: an advanced method of evaluation. J. Appl. Crystallogr. 38, 78-86 (2005).

Schmittel, M., Kalsani, V., Kishore, R. S. K., Cölfen, H. and Bats, J. W.: Dynamic and fluorescent nanoscale phenanthroline/terpyridine zinc(II) ladders. Self-recognition in unlike ligand/like metal coordination scenarios. Journal of the American Chemical Society 127, 11544-11545 (2005).

Smarsly, B., Brezesinski, T. and Antonietti, M.: Generation of functional mesoporous thin films of binary and ternary metal oxides with crystalline pore walls using novel block copolymer templates and characterization by suitable analytical techniques. Abstracts of Papers of the American Chemical Society 229, U722-U722 (2005).

Smarsly, B., Gibaud, A., Ruland, W., Sturmayr, D. and Brinker, C. J.: Quantitative SAXS analysis of oriented 2D hexagonal cylindrical silica mesostructures in thin films obtained from nonionic surfactants. Langmuir 21, 3858-3866 (2005).

Smarsly, B., Groenewolt, M. and Antonietti, M.: SAXS analysis of mesoporous model materials: a validation of data evaluation techniques to characterize pore size, shape, surface area, and curvature of the interface. Progress in Colloid and Polymer Science 130, 105-113 (2005).

Smarsly, B. and Kaper, H.: Liquid inorganic-organic nanocomposites: Novel electrolytes and ferrofluids. Angewandte Chemie-International Edition 44, 3809-3811 (2005).

Smarsly, B., Thommes, M., Ravikovitch, P. I. and Neimark, A. V.: Characterization of worm-like micro- and mesoporous silicas by small-angle scattering and high-resolution adsorption porosimetry. Adsorption-Journal of the International Adsorption Society 11, 653-655 (2005).

Szizybalski, A., Girgsdies, F., Rabis, A., Wang, Y., Niederberger, M. and Ressler, T.: In situ investigations of structure-activity relationships of a Cu/ZrO_2 catalyst for the steam reforming of methanol. J. Catal. 233, 297-307 (2005).

Tauer, K.: Stability of monomer emulsion droplets and implications for polymerizations therein. Polymer 46, 1385-1394 (2005).

Tauer, K., Ali, A. M. I. and Sedlak, M.: On the preparation of stable poly(2-hydroxyethyl methacrylate) nanoparticles. Colloid Polym. Sci. 283, 351-358 (2005).

Tauer, K., Ali, A. M. I., Yildiz, U. and Sedlak, M.: On the role of hydrophilicity and hydrophobicity in aqueous heterophase polymerization. Polymer 46, 1003-1015 (2005).

Tauer, K., Khrenov, V., Shirshova, N. and Nassif, N.: Preparation and application of double hydrophilic block copolymer particles. Macromolecular Symposia 226, 187-201 (2005).
Tauer, K., Nozari, S. and Ali, A. M. I.: Experimental reconsideration of radical entry into latex particles. Macromolecules 38, 8611-8613 (2005).

Tauer, K., Nozari, S., Ali, A. M. I. and Kozempel, S.: Sorption of hydrophobic organic compounds by aqueous latexes. Macromolecular Rapid Communications 26, 1228-1232 (2005).

ten Cate, M. G. J., Rettig, H., Bernhardt, K. and Börner, H. G.: Sequence-defined polypeptide-polymer conjugates utilizing reversible addition fragmentation transfer radical polymerization. Macromolecules 38, 10643-10649 (2005).

van Maanen, G. J., Seeley, S. L., Capracotta, M. D., White, S. A., Bukovnik, R. R., Hartmann, J., Martin, J. D. and Spontak, R. J.: Property and morphology development in nanocomposite thermoplastic elastomer gels. Langmuir 21, 3106-3115 (2005).

Viala, S., Tauer, K., Antonietti, M., Lacik, I. and Bremser, W.: Structural control in radical polymerization with 1, 1-diphenylethylene. Part 3. Aqueous heterophase polymerization. Polymer 46, 7843-7854 (2005).

Voss, R., Thomas, A., Antonietti, M. and Ozin, G. A.: Synthesis and characterization of highly amine functionalized mesoporous organosilicas by an "all-in-one" approach. J. Mater. Chem. 15, 4010-4014 (2005).

Wang, D. Y., Li, J. S., Chan, C. T., Sagueirino-Maceira, V., Liz-Marzan, L. M., Romanov, S. and Caruso, F.: Optical properties of nanoparticle-based metallodielectric inverse opals. Small 1, 122-130 (2005).

Wang, T. X., Cölfen, H. and Antonietti, M.: Nonclassical crystallization: Mesocrystals and morphology change of $CaCO_3$ crystals in the presence of a polyelectrolyte additive. Journal of the American Chemical Society 127, 3246-3247 (2005).

Wang, T. X., Rother, G. and Cölfen, H.: A new method to purify highly phosphonated block copolymers and their effect on calcium carbonate mineralization. Macromolecular Chemistry and Physics 206, 1619-1629 (2005).

Wei, Z. X., Laitinen, T., Smarsly, B., Ikkala, O. and Faul, C. F. J.: Self-assembly and electrical conductivity transitions in conjugated oligoaniline - Surfactant complexes. Angewandte Chemie-International Edition 44, 751-756 (2005).
Wohlrab, S., Cölfen, H. and Antonietti, M.: Crystalline, porous microspheres made from amino acids by using polymer-induced liquid precursor phases. Angewandte Chemie-International Edition 44, 4087-4092 (2005).

Wohlrab, S., Pinna, N., Antonietti, M. and Cölfen, H.: Polymer-induced alignment of DL-alanine nanocrystals to crystalline mesostructures. Chemistry-a European Journal 11, 2903-2913 (2005).

Xu, A. W., Yu, Q., Dong, W. F., Antonietti, M. and Cölfen, H.: Stable amorphous $CaCO_3$ microparticles with hollow spherical superstructures stabilized by phytic acid. Advanced Materials 17, 2217-2221 (2005).

Yu, S. H., Cölfen, H., Tauer, K. and Antonietti, M.: Tectonic arrangement of $BaCO_3$ nanocrystals into helices induced by a racemic block copolymer. Nature Materials 4, 51-55 (2005).

Zakrevskyy, Y., Smarsly, B., Stumpe, J. and Faul, C. F. J.: Highly ordered monodomain ionic self-assembled liquid-crystalline materials. Physical Review E 71, Art. No. 021701 (2005).

Zhang, T. R., Spitz, C., Antonietti, M. and Faul, C. F. J.: Highly photoluminescent polyoxometaloeuropate-surfactant complexes by ionic self-assembly. Chemistry-a European Journal 11, 1001-1009 (2005).

Colloid Chemistry 2006

Ahmad, H., Islam, A., Hossain, M. A., Miah, M. A. J. and Tauer, K.: Emulsion copolymerization of hydrophobic and hydrophilic monomers: an experimental study with styrene and 2-hydroxyethyl methacrylate. E-Polymers, Art. No. 30 (2006).

Antonietti, M.: Silica nanocasting of lyotropic surfactant phases and organized organic matter: material science or an analytical tool? Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences 364, 2817-2840 (2006).

Ba, J. H., Rohlfing, D. F., Feldhoff, A., Brezesinski, T., Djerdj, I., Wark, M. and Niederberger, M.: Nonaqueous synthesis of uniform indium tin oxide nanocrystals and their electrical conductivity in dependence of the tin oxide concentration. Chem. Mater. 18, 2848-2854 (2006).

Boissiere, C., Nicole, L., Gervais, C., Babonneau, F., Antonietti, M., Amenitsch, H., Sanchez, C. and Grosso, D.: Nanocrystalline mesoporous gamma-alumina powders "UPMC1 material" gathers thermal and chemical stability with high surface area. Chem. Mater. 18, 5238-5243 (2006).

Brezesinski, T., Fischer, A., Iimura, K., Sanchez, C., Grosso, D., Antonietti, M. and Smarsly, B. M.: Generation of self-assembled 3D mesostructured SnO_2 thin films with highly crystalline frameworks. Advanced Functional Materials 16, 1433-1440 (2006).

Publications/Department of Colloid Chemistry

Brezesinski, T., Groenewolt, M., Antonietti, M. and Smarsly, B.: Crystal-to-crystal phase transition in self-assembled mesoporous iron oxide films. Angewandte Chemie-International Edition 45, 781-784 (2006).

Brezesinski, T., Groenewolt, M., Gibaud, A., Pinna, N., Antonietti, M. and Smarsly, B. M.: Evaporation-induced self-assembly (EISA) at its limit: Ultrathin, crystalline patterns by templating of micellar monolayers. Advanced Materials 18, 2260-2263 (2006).

Brezesinski, T., Groenewolt, M., Pinna, N., Amenitsch, H., Antonietti, M. and Smarsly, B. M.: Surfactant-mediated generation of iso-oriented dense and mesoporous crystalline metal-oxide layers. Advanced Materials 18, 1827-1831 (2006).

Brezesinski, T., Rohlfing, D. F., Sallard, S., Antonietti, M. and Smarsly, B. M.: Highly crystalline WO_3 thin films with ordered 3D mesoporosity and improved electrochromic performance. Small 2, 1203-1211 (2006).

Cui, X. J., Antonietti, M. and Yu, S. H.: Structural effects of iron oxide nanoparticles and iron ions on the hydrothermal carbonization of starch and rice carbohydrates. Small 2, 756-759 (2006).

Diez, I., Tauer, K. and Schulz, B.: Unusual polymer dispersions-polypyrrole suspensions made of rings, frames, and platelets. Colloid Polym. Sci. 284, 1431-1442 (2006).

Dogan, A., Gunkaya, G., Suvaci, E. and Niederberger, M.: Electrophoretic deposition of nano-sized $BaTiO_3$. J. Mater. Sci. 41, 8196-8201 (2006).

Dogan, A., Gunkaya, G., Suvaci, E. and Niederberger, M.: Electrophoretic deposition of nanocrystalline $BaTiO_3$ in ethanol medium. Key Eng. Mater. 314, 133-139 (2006).

Erbe, A., Tauer, K. and Sigel, R.: Ellipsometric light scattering for the characterization of thin layers on dispersed colloidal particles. Physical Review E 73, Art. No. 031406 (2006).

Franke, D., Vos, M., Antonietti, M., Sommerdijk, N. and Faul, C. F. J.: Induced supramolecular chirality in nanostructured materials: Ionic self-assembly of perylene-chiral surfactant complexes. Chem. Mater. 18, 1839-1847 (2006).

Gao, Y. X., Yu, S. H., Cong, H. P., Jiang, J., Xu, A. W., Dong, W. F. and Cölfen, H.: Block-copolymer-controlled growth of $CaCO_3$ microrings. Journal of Physical Chemistry B 110, 6432-6436 (2006).

Garnweitner, G. and Niederberger, M.: Nonaqueous and surfactant-free synthesis routes to metal oxide nanoparticles. J. Am. Ceram. Soc. 89, 1801-1808 (2006).

Gateshki, M., Petkov, V., Hyeon, T., Joo, J., Niederberger, M. and Ren, Y.: Interplay between the local structural disorder and the length of structural coherence in stabilizing the cubic phase in nanocrystalline ZrO_2. Solid State Commun. 138, 279-284 (2006).

Geng, Y., Discher, D. E., Justynska, J. and Schlaad, H.: Grafting short peptides onto polybutadiene-block-poly(ethylene oxide): A platform for self-assembling hybrid amphiphiles. Angewandte Chemie-International Edition 45, 7578-7581 (2006).

Goettmann, F., Fischer, A., Antonietti, M. and Thomas, A.: Chemical synthesis of mesoporous carbon nitrides using hard templates and their use as a metal-free catalyst for friedel-crafts reaction of benzene. Angewandte Chemie-International Edition 45, 4467-4471 (2006).

Goettmann, F., Fischer, A., Antonietti, M. and Thomas, A.: Metal-free catalysis of sustainable Friedel-Crafts reactions: direct activation of benzene by carbon nitrides to avoid the use of metal chlorides and halogenated compounds. Chemical Communications, 4530-4532 (2006).

Hartmann, L., Krause, E., Antonietti, M. and Börner, H. G.: Solid-phase supported polymer synthesis of sequence-defined, multifunctional poly(amidoamines). Biomacromolecules 7, 1239-1244 (2006).

Hentschel, J. and Börner, H. G.: Peptide-directed microstructure formation of polymers in organic media. Journal of the American Chemical Society 128, 14142-14149 (2006).

Hentschel, J., Krause, E. and Börner, H. G.: Switch-peptides to trigger the peptide guided assembly of poly(ethylene oxide)-peptide conjugates into tape structures. Journal of the American Chemical Society 128, 7722-7723 (2006).

Holtze, C., Antonietti, M. and Tauer, K.: Ultrafast conversion and molecular weight control through temperature programming in microwave-induced miniemulsion polymerization. Macromolecules 39, 5720-5728 (2006).

Holtze, C., Sivaramakrishnan, R., Antonietti, M., Tsuwi, J., Kremer, F. and Kramer, K. D.: The microwave absorption of emulsions containing aqueous micro- and nanodroplets: A means to optimize microwave heating. J. Colloid Interface Sci. 302, 651-657 (2006).

Justynska, J., Hordyjewicz, Z. and Schlaad, H.: New functional diblock copolymers through radical addition of mercaptans. Macromolecular Symposia 240, 41-46 (2006).

Kasemi, E., Zhuang, W., Rabe, J. P., Fischer, K., Schmidt, M., Colussi, M., Keul, H., Yi, D., Cölfen, H. and Schlüter, A. D.: Synthesis of an anionically chargeable, high-molar-mass, second-generation dendronized polymer and the observation of branching by scanning force microscopy. Journal of the American Chemical Society 128, 5091-5099 (2006).

Krasia, T. and Schlaad, H.: Poly[2-(acetoacetoxy)ethyl methacrylatel-based hybrid micelles. In: Metal-Containing and Metallosupramolecular Polymers and Materials. (Ed.), ACS Symposium Series 928, 2006, 157-167.

Kuckling, D., Vo, C. D., Adler, H. J. P., Völkel, A. and Cölfen, H.: Preparation and characterization of photo-cross-linked thermosensitive PNIPAAm nanogels. Macromolecules 39, 1585-1591 (2006).

Kumar, A. S., Perez-Ramirez, J., Debbagh, M. N., Smarsly, B., Bentrup, U. and Bruckner, A.: Evidence of the vital role of the pore network on various catalytic conversions of N_2O over Fe-silicalite and Fe-SBA-15 with the same iron constitution. Applied Catalysis B-Environmental 62, 244-254 (2006).

Lutz, J. F., Börner, H. G. and Weichenhan, K.: Combining ATRP and "click" chemistry: a promising platform toward functional biocompatible polymers and polymer bioconjugates. Macromolecules 39, 6376-6383 (2006).

Ma, Y. R., Börner, H. G., Hartmann, J. and Cölfen, H.: Synthesis of DL-alanine hollow tubes and core-shell mesostructures. Chemistry-A European Journal 12, 7882-7888 (2006).

Ma, Y. R., Cölfen, H. and Antonietti, M.: Morphosynthesis of alanine mesocrystals by pH control. Journal of Physical Chemistry B 110, 10822-10828 (2006).

Publications/Department of Colloid Chemistry

Meyer-Lueckel, H., Paris, S., Mueller, J., Cölfen, H. and Kielbassa, A. M.: Influence of the application time on the penetration of different dental adhesives and a fissure sealant into artificial subsurface lesions in bovine enamel. Dental Materials 22, 22-28 (2006).

Meyer, M. and Schlaad, H.: Poly(2-isopropyl-2-oxazoline)-poly(L-glutamate) block copolymers through ammonium-mediated NCA polymerization. Macromolecules 39, 3967-3970 (2006).

Moores, A. and Goettmann, F.: The plasmon band in noble metal nanoparticles: an introduction to theory and applications. New J. Chem. 30, 1121-1132 (2006).

Niederberger, M. and Cölfen, H.: Oriented attachment and mesocrystals: Non-classical crystallization mechanisms based on nanoparticle assembly. Physical Chemistry Chemical Physics 8, 3271-3287 (2006).

Niederberger, M. and Garnweitner, G.: Organic reaction pathways in the nonaqueous synthesis of metal oxide nanoparticles. Chemistry-A European Journal 12, 7283-7302 (2006).

Niederberger, M., Garnweitner, G., Buha, J., Polleux, J., Ba, J. H. and Pinna, N.: Nonaqueous synthesis of metal oxide nanoparticles: Review and indium oxide as case study for the dependence of particle morphology on precursors and solvents. Journal of Sol-Gel Science and Technology 40, 259-266 (2006).

Okubo, T., Mizutani, T., Okamoto, J., Kimura, K., Tsuchida, A., Tauer, K., Khrenov, V., Kawaguchi, H. and Tsuji, S.: Thermo-sensitive colloidal crystals of silica spheres in the presence of large spheres with poly (N-isopropyl acrylamide) shells. Colloid Polym. Sci. 285, 351-358 (2006).

Ozer, B. H., Smarsly, B., Antonietti, M. and Faul, C. F. J.: DNA-analogous structures from deoxynucleophosphates and polylysine by ionic self-assembly. Soft Matter 2, 329-336 (2006).

Page, M. G. and Cölfen, H.: Improved control of $CaCO_3$ precipitation by direct carbon dioxide diffusion: Application in mesocrystal assembly. Crystal Growth & Design 6, 1915-1920 (2006).

Peng, Y., Xu, A. W., Deng, B., Antonietti, M. and Cölfen, H.: Polymer-controlled crystallization of zinc oxide hexagonal nanorings and disks. Journal of Physical Chemistry B 110, 2988-2993 (2006).

Petkov, V., Gateshki, M., Niederberger, M. and Ren, Y.: Atomic-scale structure of nanocrystalline $Ba_xSr_{1-x}TiO_3$ (x=1, 0.5, 0) by X-ray diffraction and the atomic pair distribution function technique. Chem. Mater. 18, 814-821 (2006).

Polleux, J., Antonietti, M. and Niederberger, M.: Ligand and solvent effects in the nonaqueous synthesis of highly ordered anisotropic tungsten oxide nanostructures. J. Mater. Chem. 16, 3969-3975 (2006).

Polleux, J., Gurlo, A., Barsan, N., Weimar, U., Antonietti, M. and Niederberger, M.: Template-free synthesis and assembly of single-crystalline tungsten oxide nanowires and their gas-sensing properties. Angewandte Chemie-International Edition 45, 261-265 (2006).

Ramirez, L. P., Antonietti, A. and Landfester, K.: Formation of novel layered nanostructures from lanthanide-complexes by secondary interactions with ligating monomers in miniemulsion droplets. Macromolecular Chemistry and Physics 207, 160-165 (2006).

Schattka, J. H., Wong, E. H. M., Antonietti, M. and Caruso, R. A.: Sol-gel templating of membranes to form thick, porous titania, titania/zirconia and titania/silica films. J. Mater. Chem. 16, 1414-1420 (2006).

Schlaad, H.: Solution properties of polypeptide-based copolymers. Advances in Polymer Science 202, 53-73 (2006).

Schlaad, H., Smarsly, B. and Below, I.: Solid-state structure of polystyrene-block-poly(Á-benzyl L-glutamate): Helix folding vs stretching. Macromolecules 39, 4631-4632 (2006).

Sel, O., Kuang, D. B., Thommes, M. and Smarsly, B.: Principles of hierarchical meso- and macropore architectures by liquid crystalline and polymer colloid templating. Langmuir 22, 2311-2322 (2006).

Sinn, C. G., Antonietti, M. and Dimova, R.: Binding of calcium to phosphatidylcholine-phosphatidylserine membranes. Colloids and Surfaces A-Physicochemical and Engineering Aspects 282, 410-419 (2006).

Sinn, C. G., Dimova, R., Huin, C., Sel, Ö. and Antonietti, M.: Binding of ion pairs onto polymer gels via dehydration entropy: A new mechanism for ion exchange. Macromolecules 39, 6310-6312 (2006).

Smarsly, B. and Antonietti, M.: Block copolymer assemblies as templates for the generation of mesoporous inorganic materials and crystalline films. European Journal of Inorganic Chemistry, 1111-1119 (2006).

Smarsly, B., Kaper, H. and Ruland, W.: On the analysis of SAXS data from oriented 2D cylindrical mesostructures measured in symmetric reflection. Nucl. Instrum. Methods Phys. Res., Sect. B 246, 249-253 (2006).

Sokolova, V., Prymak, O., Meyer-Zaika, W., Cölfen, H., Rehage, H., Shukla, A. and Epple, M.: Synthesis and characterization of DNA-functionalized calcium phosphate nanoparticles. Materialwissenschaft und Werkstofftechnik 37, 441-445 (2006).

Sonnenburg, K., Adelhelm, P., Antonietti, M., Smarsly, B., Noske, R. and Strauch, P.: Synthesis and characterization of SiC materials with hierarchical porosity obtained by replication techniques. Physical Chemistry Chemical Physics 8, 3561-3566 (2006).

Tattakhova-Rohfing, D., Brezesinski, T., Rathousky, J., Feldhoff, A., Oekermann, T., Wark, M. and Smarsly, B.: Transparent conducting films of indium tin oxide with 3D mesopore architecture. Advanced Materials 18, 2980-2983 (2006).

Tauer, K.: Hydrophilic regions inside colloidal polymer particles in water. Macromolecules 39, 2007-2009 (2006).

ten Cate, M. G. J., Severin, N. and Börner, H. G.: Self-assembling peptide-polymer conjugates comprising D-alt-L)-cyclopeptides as aggregator domains. Macromolecules 39, 7831-7838 (2006).

Thommes, M., Smarsly, B., Groenewolt, M., Ravikovitch, P. I. and Neimark, A. V.: Adsorption hysteresis of nitrogen and argon in pore networks and characterization of novel micro- and mesoporous silicas. Langmuir 22, 756-764 (2006).

Thünemann, A. F., Schütt, D., Sachse, R., Schlaad, H. and Möhwald, H.: Complexes of poly(ethylene oxide)-block-poly(L-glutamate) and diminazene. Langmuir 22, 2323-2328 (2006).

Tirrell, M. V. and Katz, A.: Self-assembly in materials synthesis. MRS Bulletin 30, 700-704 (2005).

Titirici, M. M., Antonietti, M. and Thomas, A.: A generalized synthesis of metal oxide hollow spheres using a hydrothermal approach. Chem. Mater. 18, 3808-3812 (2006).

Publications/Department of Interfaces

Tongcher, O., Sigel, R. and Landfester, K.: Liquid crystal nanoparticles prepared as miniemulsions. Langmuir 22, 4504-4511 (2006).

Wang, T. P., Antonietti, M. and Cölfen, H.: Calcite mesocrystals: "Morphing" crystals by a polyelectrolyte. Chemistry-A European Journal 12, 5722-5730 (2006).

Wang, T. W., Sel, Ö., Djerdj, I. and Smarsly, B.: Preparation of a large Mesoporous CeO_2 with crystalline walls using PMMA colloidal crystal templates. Colloid Polym. Sci. 285, 1-9 (2006).

Wang, T. X. and Cölfen, H.: In situ investigation of complex BaSO4 fiber generation in the presence of sodium polyacrylate. 1. Kinetics and solution analysis. Langmuir 22, 8975-8985 (2006).

Wang, T. X., Reinecke, A. and Cölfen, H.: In situ investigation of complex BaSO4 fiber generation in the presence of sodium polyacrylate. 2. Crystallization mechanisms. Langmuir 22, 8986-8994 (2006).

Wang, T. X., Xu, A. W. and Cölfen, H.: Formation of self-organized dynamic structure patterns of barium carbonate crystals in polymer-controlled crystallization. Angewandte Chemie-International Edition 45, 4451-4455 (2006).

Wu, C. Y., Yu, S. H. and Antonietti, M.: Complex concaved cuboctahedrons of copper sulfide crystals with highly geometrical symmetry created by a solution process. Chem. Mater. 18, 3599-3601 (2006).

Xu, A. W., Antonietti, M., Cölfen, H. and Fang, Y. P.: Uniform hexagonal plates of vaterite CaCO3 mesocrystals formed by biomimetic mineralization. Advanced Functional Materials 16, 903-908 (2006).

Yagci, Y. E., Antonietti, M. and Börner, H. G.: Synthesis of poly(tartar amides) as bio-inspired antifreeze additives. Macromolecular Rapid Communications 27, 1660-1664 (2006).

You, L. C. and Schlaad, H.: An easy way to sugar-containing polymer vesicles or glycosomes. Journal of the American Chemical Society 128, 13336-13337 (2006).

Zickler, G. A., Smarsly, B., Gierlinger, N., Peterlik, H. and Paris, O.: A reconsideration of the relationship between the crystallite size L-a of carbons determined by X-ray diffraction and Raman spectroscopy. Carbon 44, 3239-3246 (2006).

Patents 2006:

Markus Antonietti
Ionenaustausch und Entsalzung durch Ionenpaarbindung an reversibel, schwach dehydratisierten Polymergelen (2006).

Markus Antonietti, Bernd Smarsly, Philipp Adelhelm, Karin Cabrera
Synthesis of porous carbon with adjustable hierarchical porosity by templating of carbon precursors with linear hydrophobic polymers (2006).

Markus Antonietti, Bernd Smarsly, Philipp Adelhelm, Joachim Maier, Sarmimala Hore, Yongsheng Hu: Herstellung graphitischer Kohlenstoffe mit hierarchischer Porosität und deren Einsatz als Anode in Batteriematerialien mit höchster Speicherdichte und verbesserter Lade/Entladecharakteristik (2006).

Interfaces 2005

Akcakayiran, D., Kurth, D. G., Rohrs, S., Rupprechter, G. and Findenegg, G. H.: Self-assembly of a metallosupramolecular coordination polyelectrolyte in the pores of SBA-15 and MCM-41 silica. Langmuir 21, 7501-7506 (2005).

Alonso, C., Bringezu, F., Brezesinski, G., Waring, A. J. and Zasadzinski, J. A.: Modifying calf lung surfactant by hexadecanol. Langmuir 21, 1028-1035 (2005).

Alvarez, C., Nogales, A., Garcia-Gutierrez, M. C., Sanz, A., Denchev, Z., Funari, S. S., Bruix, M. and Ezquerra, T. A.: Confined crystallization in phase-separated poly(ethylene terephthalate)/poly(ethylene naphthalene 2,6-dicarboxilate) blends. European Physical Journal E 18, 459-465 (2005).

An, Z. H., Tao, C., Lu, G., Möhwald, H., Zheng, S. P., Cui, Y. and Li, J. B.: Fabrication and characterization of human serum albumin and L-alpha-dimyristoylphosphatidic acid microcapsules based on template technique. Chem. Mater. 17, 2514-2519 (2005).

Balabushevich, N. G., Sukhorukov, G. B. and Larionova, N. I.: Polyelectrolyte multilayer microspheres as carriers for bienzyme system: Preparation and characterization. Macromolecular Rapid Communications 26, 1168-1172 (2005).

Beinhoff, M., Weigel, W., Rettig, W., Bruedgam, I., Hartl, H. and Schlueter, A. D.: Phenylene alkylene dendrons with site-specific incorporated fluorescent pyrene probes. J. Org. Chem. 70, 6583-6591 (2005).

Bodenthin, Y., Pietsch, U., Grenzer, J., Geue, T., Möhwald, H. and Kurth, D. G.: Structure and temperature behavior of metallo-supramolecular assemblies. Journal of Physical Chemistry B 109, 12795-12799 (2005).

Bodenthin, Y., Pietsch, U., Möhwald, H. and Kurth, D. G.: Inducing spin crossover in metallo-supramolecular polyelectrolytes through an amphiphilic phase transition. Journal of the American Chemical Society 127, 3110-3114 (2005).

Bozano, L. D., Kean, B. W., Beinhoff, M., Carter, K. R., Rice, P. M. and Scott, J. C.: Organic materials and thin-film structures for cross-point memory cells based on trapping in metallic nanoparticles. Advanced Functional Materials 15, 1933-1939 (2005).

Chen, X. D., Wiehle, S., Chi, L. F., Muck-Lichtenfeld, C., Rudert, R., Vollhardt, D., Fuchs, H. and Haufe, G.: Phase behavior of 2,3-disubstituted methyl octadecanoate monolayers at the air-water interface. Langmuir 21, 3376-3383 (2005).

Chen, X. D., Wiehle, S., Weygand, M., Brezesinski, G., Klenz, U., Galla, H. J., Fuchs, H., Haufe, G. and Chi, L. F.: Unconventional air-stable interdigitated bilayer formed by 2,3-disubstituted fatty acid methyl esters. Journal of Physical Chemistry B 109, 19866-19875 (2005).

Ciunel, K., Armelin, M., Findenegg, G. H. and Klitzing, R. v.: Evidence of surface charge at the air/water interface from thin-film studies on polyelectrolyte-coated substrates. Langmuir 21, 4790-4793 (2005).

Dai, Z. F., Meiser, F. and Möhwald, H.: Nanoengineering of iron oxide and iron oxide/silica hollow spheres by sequential layering combined with a sol-gel process. J. Colloid Interface Sci. 288, 298-300 (2005).

De Geest, B. G., Dejugnat, C., Sukhorukov, G. B., Braeckmans, K., De Smedt, S. C. and Demeester, J.: Self-rupturing microcapsules. Advanced Materials 17, 2357-2361 (2005).

Dejugnat, C., Halozan, D. and Sukhorukov, G. B.: Defined picogram dose inclusion and release of macromolecules using polyelectrolyte microcapsules. Macromolecular Rapid Communications 26, 961-967 (2005).

Delajon, C., Gutberlet, T., Steitz, R., Möhwald, H. and Krastev, R.: Formation of polyelectrolyte multilayer architectures with embedded DMPC studied in situ by neutron reflectometry. Langmuir 21, 8509-8514 (2005).

Dong, W. F., Ferri, J. K., Adalsteinsson, T., Schönhoff, M., Sukhorukov, G. B. and Möhwald, H.: Influence of shell structure on stability, integrity, and mesh size of polyelectrolyte capsules: Mechanism and strategy for improved preparation. Chem. Mater. 17, 2603-2611 (2005).

Dong, W. F., Liu, S. Q., Wan, L., Mao, G. Z., Kurth, D. G. and Möhwald, H.: Controlled permeability in polyelectrolyte films via solvent treatment. Chem. Mater. 17, 4992-4999 (2005).

Duan, H. W., Kuang, M., Wang, D. Y., Kurth, D. G. and Möhwald, H.: Colloidally stable amphibious nanocrystals derived from poly { 2-(dimethylamino)ethyl methaerylatel capping. Angewandte Chemie-International Edition 44, 1717-1720 (2005).

Duan, H. W., Wang, D. Y., Sobal, N. S., Giersig, M., Kurth, D. G. and Möhwald, H.: Magnetic colloidosomes derived from nanoparticle interfacial self-assembly. Nano Letters 5, 949-952 (2005).

Dunne, G., McDonnell, L., Miller, R., McMillan, N. D., O'Rourke, B. and Mitchell, C. I.: Optical monitoring of proteins at solid interfaces. In: Proceedings of Opto Ireland 2005: Nanotechnology and Nanophotonics. (Ed.) W. J. Blau, D. Kennedy and J. Correavy, Proceedings of the SPIE 5824, SPIE, Bellingham 2005, 199-204.

Ezquerra, T. A., Martinez-Gomez, A., Alvarez, C., Alonso, E., Sanz, A., Garcia-Gutierrez, M. C., Bello, A., Perez, E., Funari, S. S. and Dommach, M.: Structure-dynamics relationship during the amorphous to smectic transition of a main chain liquid crystalline polymer. J. Non-Cryst. Solids 351, 2768-2772 (2005).

Fainerman, V. B., Leser, M. E., Michel, M., Lucassen-Reynders, E. H. and Miller, R.: Kinetics of the desorption of surfactants and proteins from adsorption layers at the solution/air interface. Journal of Physical Chemistry B 109, 9672-9677 (2005).

Fainerman, V. B. and Miller, R.: Equilibrium and dynamic characteristics of protein adsorption layers at gas-liquid interfaces: Theoretical and experimental data. Colloid Journal 67, 393-404 (2005).

Fainerman, V. B., Vollhardt, D., Aksenenko, E. V. and Liu, F.: Molecular recognition kinetics of non-surface active pyrimidine derivatives dissolved in the aqueous subphase by an amphiphilic melamine type monolayer: A theoretical approach. Journal of Physical Chemistry B 109, 14137-14143 (2005).

Fang, Y. P., Xu, A. W. and Dong, W. F.: Highly improved green photoluminescence from $CePO_4$: $Tb/LaPO_4$ core/shell nanowires. Small 1, 967-971 (2005).

Ferri, J. K., Dong, W. F. and Miller, R.: Ultrathin free-standing polyelectrolyte nanocomposites: A novel method for preparation and characterization of assembly dynamics. Journal of Physical Chemistry B 109, 14764-14768 (2005).

Publications/Department of Interfaces

Ferri, J. K., Miller, R. and Makievski, A. V.: Equilibrium and dynamics of PEO/PPO/PEO penetration into DPPC monolayers. Colloids and Surfaces A-Physicochemical and Engineering Aspects 261, 39-48 (2005).

Fudickar, W., Fery, A. and Linker, T.: Reversible light and air-driven lithography by singlet oxygen. Journal of the American Chemical Society 127, 9386-9387 (2005).

Funari, S. S., Prades, J., Escriba, P. V. and Barcelo, F.: Farnesol and geranylgeraniol modulate the structural properties of phosphatidylethanolamine model membranes. Molecular Membrane Biology 22, 303-311 (2005).

Gao, C. Y., Möhwald, H. and Shen, J. C.: Thermosensitive poly (allylamine)-g-poly (N-isopropylacrylamide): synthesis, phase separation and particle formation. Polymer 46, 4088-4097 (2005).

Georgieva, R., Dimova, R., Sukhorukov, G., Ibarz, G. and Möhwald, H.: Influence of different salts on micro-sized polyelectrolyte hollow capsules. J. Mater. Chem. 15, 4301-4310 (2005).

Georgieva, R., Moya, S. E., Bäumler, H., Möhwald, H. and Donath, E.: Controlling ionic conductivity in lipid polyelectrolyte composite capsules by cholesterol. Journal of Physical Chemistry B 109, 18025-18030 (2005).

Gong, Y. J., Gao, M. Y., Wang, D. Y. and Möhwald, H.: Incorporating fluorescent CdTe nanocrystals into a hydrogel via hydrogen bonding: Toward fluorescent microspheres with temperature-responsive properties. Chem. Mater. 17, 2648-2653 (2005).

Grigorieva, O. V., Grigoriev, D. O., Kovalchuk, N. M. and Vollhardt, D.: Auto-oscillation of surface tension: heptanol in water and water/ethanol systems. Colloids and Surfaces A-Physicochemical and Engineering Aspects 256, 61-68 (2005).

Halozan, D., Dejugnat, C., Brumen, M. and Sukhorukov, G. B.: Entrapment of a weak polyanion and H^+/Na^+ exchange in confined polyelectrolyte microcapsules. Journal of Chemical Information and Modeling 45, 1589-1592 (2005).

Heuberger, R., Sukhorukov, G., Vörös, J., Textor, M. and Möhwald, H.: Biofunctional polyelectrolyte multilayers and microcapsules: Control of non-specific and bio-specific protein adsorption. Advanced Functional Materials 15, 357-366 (2005).

Heuvingh, J., Zappa, M. and Fery, A.: Salt softening of polyelectrolyte multilayer capsules. Langmuir 21, 3165-3171 (2005).

Iyota, H., Krastev, R. and Müller, H. J.: Thermodynamic studies on thin liquid films. III: Miscibility in adsorbed films at film interfaces. Colloid Polym. Sci. 283, 975-981 (2005).

Khattari, Z., Ruschel, Y., Wen, H. Z., Fischer, A. and Fischer, T. M.: Compactification of a myelin mimetic Langmuir monolayer upon adsorption and unfolding of myelin basic protein. Journal of Physical Chemistry B 109, 3402-3407 (2005).

Khopade, A. J., Arulsudar, N., Khopade, S. A., Knocke, R., Hartmann, A. and Möhwald, H.: From ultrathin capsules to biaqueous vesicles. Biomacromolecules 6, 3433-3439 (2005).

Khopade, A. J. and Möhwald, H.: Pseudobilayer vesicle formation via layer-by-layer assembly of hydrophobically modified polymers on sacrificial substrates. Advanced Functional Materials 15, 1088-1094 (2005).

Khopade, A. J. and Möhwald, H.: Statistical megamer morphologies and materials from PAMAM dendrimers. Macromolecular Rapid Communications 26, 445-449 (2005).

Kirchner, C., Javier, A. M., Susha, A. S., Rogach, A. L., Kreft, O., Sukhorukov, G. B. and Parak, W. J.: Cytotoxicity of nanoparticle-loaded polymer capsules. Talanta 67, 486-491 (2005).

Klitzing, R. v.: Effect of interface modification on forces in foam films and wetting films. Adv. Colloid Interface Sci. 114, 253-266 (2005).

Knufing, L., Schollmeyer, H., Riegler, H. and Mecke, K.: Fractal analysis methods for solid alkane monolayer domains at SiO_2/air interfaces. Langmuir 21, 992-1000 (2005).

Koelsch, P. and Motschmann, H.: Varying the counterions at a charged interface. Langmuir 21, 3436-3442 (2005).

Koelsch, P. and Motschmann, H.: Relating foam lamella stability and surface dilational rheology. Langmuir 21, 6265-6269 (2005).

Köhler, K., Shchukin, D. G., Möhwald, H. and Sukhorukov, G. B.: Thermal behavior of polyelectrolyte multilayer microcapsules. 1. The effect of odd and even layer number. Journal of Physical Chemistry B 109, 18250-18259 (2005).

Kolln, K., Grotkopp, I., Burghammer, M., Roth, S. V., Funari, S. S., Dommach, M. and Muller, M.: Mechanical properties of cellulose fibres and wood. Orientational aspects in situ investigated with synchrotron radiation. Journal of Synchrotron Radiation 12, 739-744 (2005).

Kovalchuk, N. A. and Vollhardt, D.: Effect of buoyancy on appearance and characteristics of surface tension repeated auto-oscillations. Journal of Physical Chemistry B 109, 15037-15047 (2005).

Kovalchuk, N. M. and Vollhardt, D.: Nonlinear spontaneous oscillations at the liquid/liquid interface produced by surfactant dissolution in the bulk phase. Journal of Physical Chemistry B 109, 22868-22875 (2005).

Kovalchuk, V. I., Makievski, A. V., Krägel, J., Pandolfini, P., Loglio, G., Liggieri, L., Ravera, F. and Miller, R.: Film tension and dilational film rheology of a single foam bubble. Colloids and Surfaces A-Physicochemical and Engineering Aspects 261, 115-121 (2005).

Kovalchuk, V. I., Miller, R., Fainerman, V. B. and Loglio, G.: Dilational rheology of adsorbed surfactant layers - role of the intrinsic two-dimensional compressibility. Adv. Colloid Interface Sci. 114, 303-312 (2005).

Kovalchuk, V. I. and Vollhardt, D.: Ion redistribution and meniscus stability at Langmuir monolayer deposition. Adv. Colloid Interface Sci. 114, 267-279 (2005).

Krägel, J., Kovalchuk, V. I., Makievski, A. V., Simoncini, M., Ravera, F., Liggieri, L., Loglio, G. and Miller, R.: Analysis of amplitude- and phase-frequency characteristics of oscillating bubble system with closed measuring cell. Microgravity science and technology 16, 186-190 (2005).

Krastev, R., Steitz, R., Gutberlet, T., Klosgen, B., Mishra, N. C. and Möhwald, H.: Lipid membranes on hydrophilic polymer cushions. Biophys. J. 88, 5A-5A (2005).

Krol, S., Nolte, M., Diaspro, A., Mazza, D., Magrassi, R., Gliozzi, A. and Fery, A.: Encapsulated living cells on microstructured surfaces. Langmuir 21, 705-709 (2005).

Kuang, M., Wang, D. Y., Bao, H. B., Gao, M. Y., Möhwald, H. and Jiang, M.: Fabrication of multicolor-encoded microspheres by tagging semiconductor nanocrystals to hydrogel spheres. Advanced Materials 17, 267-270 (2005).

Publications/Department of Interfaces

Kuang, M., Wang, D. Y., Gao, M. Y., Hartmarm, J. and Möhwald, H.: A bio-inspired route to fabricate submicrometer-sized particles with unusual shapes - Mineralization of calcium carbonate within hydrogel spheres. Chem. Mater. 17, 656-660 (2005).

Kuang, M., Wang, D. Y. and Möhwald, H.: Fabrication of thermoresponsive plasmonic microspheres with long-term stability from hydrogel spheres. Advanced Functional Materials 15, 1611-1616 (2005).

Kubowicz, S., Baussard, J. F., Lutz, J. F., Thünemann, A. F., von Berlepsch, H. and Laschewsky, A.: Multicompartment micelles formed by self-assembly of linear ABC triblock copolymers in aqueous medium. Angewandte Chemie-International Edition 44, 5262-5265 (2005).

Kubowicz, S., Thünemann, A. F., Weberskirch, R. and Möhwald, H.: Cylindrical micelles of alpha-fluorocarbon-omega-hydrocarbon end-capped poly(N-acylethylene imine)s. Langmuir 21, 7214-7219 (2005).

Kurth, D. G., Lopez, J. P. and Dong, W. F.: A new Co(II)-metalloviologen-based electrochromic material integrated in thin multilayer films. Chemical Communications, 2119-2121 (2005).

Laschewsky, A., Lunkenheimer, K., Rakotoaly, R. H. and Wattebled, L.: Spacer effects in dimeric cationic surfactants. Colloid Polym. Sci. 283, 469-479 (2005).

Lazar, P.: Transport mechanisms and wetting dynamics in molecularly thin films of long-chain alkanes at solid/vapour interface: relation to the solid-liquid phase transition. Potsdam 2005.

Lazar, P. and Riegler, H.: Reversible self-propelled droplet movement: A new driving mechanism. Phys. Rev. Lett. 95, Art. No. 136103 (2005).

Lazar, P., Schollmeyer, H. and Riegler, H.: Spreading and two-dimensional mobility of long-chain alkanes at solid/gas interfaces. Phys. Rev. Lett. 94, Art. No. 116101 (2005).

Lehmann, P., Symietz, C., Brezesinski, G., Krass, H. and Kurth, D. G.: Langmuir and Langmuir-Blodgett films of metallosupramolecular polyelectrolyte-amphiphile complexes. Langmuir 21, 5901-5906 (2005).

Leporatti, S., Sczech, R., Riegler, H., Bruzzano, S., Storsberg, J., Loth, F., Jaeger, W., Laschewsky, A., Eichhorn, S. and Donath, E.: Interaction forces between cellulose microspheres and ultrathin cellulose films monitored by colloidal probe microscopy - effect of wet strength agents. J. Colloid Interface Sci. 281, 101-111 (2005).

Leser, M. E., Acquistapace, S., Cagna, A., Makievski, A. V. and Miller, R.: Limits of oscillation frequencies in drop and bubble shape tensiometry. Colloids and Surfaces A-Physicochemical and Engineering Aspects 261, 25-28 (2005).

Li, J. B., Möhwald, H., An, Z. H. and Lu, G.: Molecular assembly of biomimetic microcapsules. Soft Matter 1, 259-264 (2005).

Li, L. D. and Möhwald, H.: Photoinduced polymerization in the wall of hollow capsules. Macromolecular Materials and Engineering 290, 843-847 (2005).

Li, L. D., Möhwald, H., Spitz, C., von Seggern, D., Mucke, M. and Menzel, R.: Long-lived photoinduced charge separation inside polarity gradient capsules. Advanced Materials 17, 2247-2249 (2005).

Liggieri, L. and Miller, R.: A Collection of Papers from the International Workshop on Bubble and Drop Interfaces, Genoa, Italy, 25-28 April, 2004 - Foreword. Adv. Colloid Interface Sci. 117, 1-1 (2005).

Liggieri, L., Ravera, F., Ferrari, M., Passerone, A., Loglio, G., Miller, R., Krägel, J. and Makievski, A. V.: Preliminary results of the facility for adsorption and surface tension (FAST) experiments onboard STS-107, in the framework of the project FASES. Microgravity science and technology 16, 196-200 (2005).

Liggieri, L., Ravera, F., Ferrari, M., Passerone, A., Loglio, G., Pandolfini, P., Steinchen, A., Sanfeld, A., Antoni, M., Clausse, D., Komjuner, L., Gomez, F., Miller, R., Makievski, A., Krägel, J., Kovalchuk, V. I., Noik, C., Dalmazzone, C., del Gaudio, L. and Di Lullo, A.: Microgravity as a tool for fundamental and applied studies on emulsion stability. In: Microgravity applications programme: successful teaming of science and industry. (Ed.) A. Wilson, European Space Agency, Noordwijk 2005, 150-167.

Liu, X. Y., Gao, C. Y., Shen, J. C. and Möhwald, H.: Multilayer microcapsules as anti-cancer drug delivery vehicle: Deposition, sustained release, and in vitro bioactivity. Macromolecular Bioscience 5, 1209-1219 (2005).

Loglio, G., Pandolfini, P., Miller, R., Makievski, A., Krägel, J., Ravera, F. and Liggieri, L.: STS-107 OV-102 mission - FAST experiment: slow surface relaxation at the solution-air interface. Microgravity science and technology 16, 205-209 (2005).

Loglio, G., Pandolfini, P., Miller, R., Makievski, A. V., Kargel, J., Ravera, F. and Noskov, B. A.: Perturbation-response relationship in liquid interfacial systems: non-linearity assessment by frequency-domain analysis. Colloids and Surfaces A-Physicochemical and Engineering Aspects 261, 57-63 (2005).

Lopez, J. P., Kraus, W., Reck, G., Thünemann, A. and Kurth, D. G.: Synthesis, structure and reactivity of the homoleptic iron(II) complex of the novel 4 '-(4 '''-pyridyl-N-oxide)-2,2 ': 6 ',2 ''-terpyridine ligand. Inorg. Chim. Acta 358, 3384-3390 (2005).

Lopez, J. S., Kraus, W., Reck, G., Thünemann, A. and Kurth, D. G.: Alternating perpendicular 1-D channels in the supramolecular structure of the copper(II) complex $[Cu(pyterpy)_2](PF_6)_2$. CH_3OH. 0.5 CH_2Cl_2 (pyterpy=4 '-(4 '''-pyridyl)-2,2': 6 ',2 ''-terpyridine). Inorganic Chemistry Communications 8, 281-284 (2005).

Makievski, A. V., Fainerman, V. B. and Miller, R.: Neues Blasendrucktensiometer zur Messung der dynamischen Oberflächenspannung von Flüssigkeiten. Labor Praxis 29, 54, 59-60 (2005).

Makievski, A. V., Kovalchuk, V. I., Krägel, J., Simoncini, M., Liggieri, L., Ferrari, M. and Pandolfini, P.: Rheological studies with spherically shaped thin liquid films. Microgravity science and technology 16, 215-218 (2005).

Maldonado-Valderrama, J., Fainerman, V. B., Aksenenko, E., Galvez-Ruiz, M. J., Cabrerizo-Vilchez, M. A. and Miller, R.: Dynamics of protein adsorption at the oil-water interface: comparison with a theoretical model. Colloids and Surfaces A-Physicochemical and Engineering Aspects 261, 85-92 (2005).

Maldonado-Valderrama, J., Fainerman, V. B., Galvez-Ruiz, M. J., Martin-Rodriguez, A., Cabrerizo-Vilchez, M. A. and Miller, R.: Dilatational rheology of beta-casein adsorbed layers at liquid-fluid interfaces. Journal of Physical Chemistry B 109, 17608-17616 (2005).

Maltseva, E., Kerth, A., Blume, A., Möhwald, H. and Brezesinski, G.: Adsorption of amyloid beta (1-40) peptide at phospholipid monolayers. Chembiochem 6, 1817-1824 (2005).

Publications/Department of Interfaces

Miller, R. and Fainerman, V. B.: Thermodynamics and kinetics of protein/surfactant mixtures adsorbed at liquid interfaces. In: Molecular interfacial phenomena of polymers and biopolymers. (Ed.) P. Chen, Woodhead Publ. Ltd., 2005, 1-45.

Miller, R., Fainerman, V. B., Kovalchuk, V. I. and Loglio, G.: Dilational surface rheology of adsorbed surfactant layers. In: Surfactants and disperse systems in theory and practice. (Ed.) K. A. Wilk, Polanica Zdrój, 2005, 71-78.

Miller, R., Grigoriev, D. O., Kragel, J., Makievski, A., Maldonado-Valderrama, J., Leser, M., Michel, A. and Fainerman, V. B.: Experimental studies on the desorption of adsorbed proteins from liquid interfaces. Food Hydrocolloids 19, 479-483 (2005).

Miller, R., Leser, M. E., Michel, M. and Fainerman, V. B.: Surface dilational rheology of mixed beta-lactoglobulin/surfactant layers at the air/water interface. Journal of Physical Chemistry B 109, 13327-13331 (2005).

Mirska, D., Schirmer, K., Funari, S. S., Langer, A., Dobner, B. and Brezesinski, G.: Biophysical and biochemical properties of a binary lipid mixture for DNA transfection. Colloids and Surfaces B-Biointerfaces 40, 51-59 (2005).

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

Möhwald, H.: EUCHEM: Nanoscale surface self-assembly. Angewandte Chemie-International Edition 44, 5920-5921 (2005).

Mueller, R., Köhler, K., Weinkamer, R., Sukhorukov, G. and Fery, A.: Melting of PDADMAC/PSS capsules investigated with AFM force spectroscopy. Macromolecules 38, 9766-9771 (2005).

Muller, A., Pope, M. T., Merca, A., Bogge, H., Schmidtmann, M., van Slageren, J., Dressel, M. and Kurth, D. G.: A small cavity with reactive internal shell atoms spanned by four {As(W/V)(9)}-type building blocks allows host-guest chemistry under confined conditions. Chemistry-a European Journal 11, 5849-5854 (2005).

Muruganathan, R. M., Müller, H. J., Möhwald, H. and Krastev, R.: Effect of headgroup size on permeability of newton black films. Langmuir 21, 12222-12228 (2005).

Nakanishi, T., Schmitt, W., Michinobu, T., Kurth, D. G. and Ariga, K.: Hierarchical supramolecular fullerene architectures with controlled dimensionality. Chemical Communications, 5982-5984 (2005).

Nolte, M., Schoeler, B., Peyratout, C. S., Kurth, D. G. and Fery, A.: Filled microcavity arrays produced by polyelectrolyte multilayer membrane transfer. Advanced Materials 17, 1665-1669 (2005).

Noskov, B. A., Akentiev, A. V., Bilibin, A. Y., Grigoriev, D. O., Loglio, G., Zorin, I. M. and Miller, R.: Adsorption kinetics of non-ionic polymers: an ellipsometric study. Mendeleev Commun., 198-200 (2005).

Noskov, B. A., Akentiev, A. V., Grigoriev, D. O., Loglio, G. and Miller, R.: Ellipsometric study of nonionic polymer solutions. J. Colloid Interface Sci. 282, 38-45 (2005).

Noskov, B. A., Loglio, G. and Miller, R.: Interaction between sodium poly(styrene sulfonate) and dodecyltrimethylammonium bromide at the air/water interface. Mendeleev Commun., 63-65 (2005).

Petrov, A. I., Volodkin, D. V. and Sukhorukov, G. B.: Protein-calcium carbonate coprecipitation: A tool for protein encapsulation. Biotechnology Progress 21, 918-925 (2005).

Petrov, J. G., Andreeva, T. D., Kurth, D. G. and Möhwald, H.: Negative dipole potentials of uncharged Langmuir monolayers due to fluorination of the hydrophilic heads. Journal of Physical Chemistry B 109, 14102-14111 (2005).

Pilakowska-Pietras, D., Lunkenheimer, K., Piasecki, A. and Pietras, M.: Adsorption behavior of surface chemically pure N-cycloalkylaldonamides at the air/water interface. Langmuir 21, 4016-4023 (2005).

Prado, L., Ponce, M. L., Funari, S. S., Schulte, K., Garamus, V. M., Willumeit, R. and Nunes, S. P.: SAXS/WAXS characterization of proton-conducting polymer membranes containing phosphomolybdic acid. J. Non-Cryst. Solids 351, 2194-2199 (2005).

Raudenkolb, S., Wartewig, S., Brezesinski, G., Funari, S. S. and Neubert, R. H. H.: Hydration properties of N-(alpha-hydroxyacyl)-sphingosine: X-ray powder diffraction and FT-Raman spectroscopic studies. Chem. Phys. Lipids 136, 13-22 (2005).

Rocha, S., Krastev, R., Thünemann, A. F., Pereira, M. C., Möhwald, H. and Brezesinski, G.: Adsorption of amyloid beta-peptide at polymer surfaces: A neutron reflectivity study. Chemphyschem 6, 2527-2534 (2005).

Rocha, S., Thünemann, A. F., Pereira, M. C., Coelho, M. A. N., Möhwald, H. and Brezesinski, G.: The conformation of B18 peptide in the presence of fluorinated and alkylated nanoparticles. Chembiochem 6, 280-283 (2005).

Russell, J. T., Lin, Y., Boker, A., Su, L., Carl, P., Zettl, H., He, J. B., Sill, K., Tangirala, R., Emrick, T., Littrell, K., Thiyagarajan, P., Cookson, D., Fery, A., Wang, Q. and Russell, T. P.: Self-assembly and cross-linking of bionanoparticles at liquid-liquid interfaces. Angewandte Chemie-International Edition 44, 2420-2426 (2005).

Safouane, M., Miller, R. and Möhwald, H.: Surface viscoelastic properties of floating polyelectrolyte multilayers films: A capillary wave study. J. Colloid Interface Sci. 292, 86-92 (2005).

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

Schulze-Schlarmann, J., Stubenrauch, C. and Miller, R.: Revision of the adsorption behavior of the non-ionic surfactant tetraoxyethylene decylether $C_{10}E_4$ at the water/air interface. Tenside Surfactants Detergents 42, 307-312 (2005).

Shchukin, D. and Sviridov, D. V.: Nanoengineered composites based on conducting polymers. In: Progress in electrochemistry research. (Ed.) M. Nunez, Nova Science Publishers, 2005, 91-121.

Shchukin, D. G., Köhler, K., Möhwald, H. and Sukhorukov, G. B.: Gas-filled polyelectrolyte capsules. Angewandte Chemie-International Edition 44, 3310-3314 (2005).

Shchukin, D. G. and Möhwald, H.: Urea photosynthesis inside polyelectrolyte capsules: Effect of confined media. Langmuir 21, 5582-5587 (2005).

Shchukin, D. G., Sukhorukov, G. B., Price, R. R. and Lvov, Y. M.: Halloysite nanotubes as biomimetic nanoreactors. Small 1, 510-513 (2005).

Shchukin, D. G., Ustinovich, E. A., Sukhorukov, G. B., Möhwald, H. and Sviridov, D. V.: Metallized polyelectrolyte microcapsules. Advanced Materials 17, 468-472 (2005).

Shchukin, D. G., Yaremchenko, A. A., Ferreira, M. G. S. and Kharton, V. V.: Polymer gel templating synthesis of nanocrystalline oxide anodes. Chem. Mater. 17, 5124-5129 (2005).

Shenoy, D. B. and Sukhorukov, G. B.: Microgel-based engineered nanostructures and their applicability with template-directed layer-by-layer polyelectrolyte assembly in protein encapsulation. Macromolecular Bioscience 5, 451-458 (2005).

Siegel, S., Vollhardt, D. and Cadenhead, D. A.: Effect of the hydroxy group position on the monolayer characteristics of hydroxypalmitic acids. Colloids and Surfaces A-Physicochemical and Engineering Aspects 256, 9-15 (2005).

Skirtach, A. G., Dejugnat, C., Braun, D., Susha, A. S., Rogach, A. L., Parak, W. J., Möhwald, H. and Sukhorukov, G. B.: The role of metal nanoparticles in remote release of encapsulated materials. Nano Letters 5, 1371-1377 (2005).

Song, R. Q., Xu, A. W., Deng, B. and Fang, Y. P.: Novel multilamellar mesostructured molybdenum oxide nanofibers and nanobelts: Synthesis and characterization. Journal of Physical Chemistry B 109, 22758-22766 (2005).

Stubenrauch, C., Fainerman, V. B., Aksenenko, E. V. and Miller, R.: Adsorption behavior and dilational rheology of the cationic alkyl trimethylammonium bromides at the water/air interface. Journal of Physical Chemistry B 109, 1505-1509 (2005).

Sukhorukov, G., Fery, A. and Möhwald, H.: Intelligent micro- and nanocapsules. Progress in Polymer Science 30, 885-897 (2005).

Sukhorukov, G. B., Rogach, A. L., Zebli, B., Liedl, T., Skirtach, A. G., Köhler, K., Antipov, A. A., Gaponik, N., Susha, A. S., Winterhalter, M. and Parak, W. J.: Nanoengineered polymer capsules: Tools for detection, controlled delivery, and site-specific manipulation. Small 1, 194-200 (2005).

Swamy, V., Kuznetsov, A., Dubrovinsky, L. S., Caruso, R. A., Shchukin, D. G. and Muddle, B. C.: Finite-size and pressure effects on the Raman spectrum nanocrystalline anatase TiO2. Physical Review B 71, Art. No. 184302 (2005).

Talapin, D. V., Shevchenko, E. V., Gaponik, N., Radtchenko, I. L., Kornowski, A., Haase, M., Rogach, A. L. and Weller, H.: Reply: Self-assembly of monodisperse nanocrystals into faceted crystal superlattices. Advanced Materials 17, 1325-1329 (2005).

Tanaka, M., Rehfeldt, F., Schneider, M. F., Gege, C., Schmidt, R. R. and Funari, S. S.: Oligomer-to-polymer transition in short ethylene glycol chains connected to mobile hydrophobic anchors. Chemphyschem 6, 101-109 (2005).

Thirumoorthy, K., Nandi, N. and Vollhardt, D.: Role of electrostatic interactions for the domain shapes of Langmuir monolayers of monoglycerol amphiphiles. Journal of Physical Chemistry B 109, 10820-10829 (2005).

Toca-Herrera, J. L., Krastev, R., Bosio, V., Kupcu, S., Pum, D., Fery, A., Sara, M. and Sleytr, U. B.: Recrystallization of bacterial S-layers on flat polyelectrolyte surfaces and hollow polyelectrolyte capsutes. Small 1, 339-348 (2005).

Tong, W. J., Dong, W. F., Gao, C. Y. and Möhwald, H.: Charge-controlled permeability of polyelectrolyte microcapsules. Journal of Physical Chemistry B 109, 13159-13165 (2005).

Tong, W. J., Dong, W. F., Gao, C. Y. and Möhwald, H.: Multilayer capsules with cell-like topology: Fabrication and spontaneous loading of various substances in aqueous and ethanol solutions. Macromolecular Chemistry and Physics 206, 1784-1790 (2005).

Tong, W. J., Gao, C. Y. and Möhwald, H.: Manipulating the properties of polyelectrolyte microcapsules by glutaraldehyde cross-linking. Chem. Mater. 17, 4610-4616 (2005).

Turkenburg, D. H., Antipov, A. A., Thathagar, M. B., Rothenberg, G., Sukhorukov, G. B. and Eiser, E.: Palladium nanoclusters in microcapsule membranes: From synthetic shells to synthetic cells. Physical Chemistry Chemical Physics 7, 2237-2240 (2005).

Uhrikova, D., Hanulova, M., Funari, S. S., Khusainova, R. S., Sersen, F. and Balgavy, P.: The structure of DNA-DOPC aggregates formed in presence of calcium and magnesium ions: A small-angle synchrotron X-ray diffraction study. Biochimica et Biophysica Acta-Biomembranes 1713, 15-28 (2005).

Uhrikova, D., Zajac, I., Dubnickova, M., Pisarcik, M., Funari, S. S., Rapp, G. and Balgavy, P.: Interaction of gemini surfactants butane-1,4-diyl-bis (alkyldimethylammonium bromide) with DNA. Colloids and Surfaces B-Biointerfaces 42, 59-68 (2005).

Ustinovich, E. A., Shchukin, D. G. and Sviridov, D. V.: Heterogeneous photocatalysis in titania-stabilized perfluorocarbon-in-water emulsions: Urea photosynthesis and chloroform photodegradation. Journal of Photochemistry and Photobiology a-Chemistry 175, 249-252 (2005).

Vignes-Adler, M., Weaire, D. and Miller, R.: Special issue - A Collection of Papers Presented at the 5th European Conference on Foams, Emulsions, and Applications, EUFOAM 2004, University of Marne-la-Vallee, Champs sur Marne (France), 5th-8th July, 2004 - Foreword. Colloids and Surfaces A-Physicochemical and Engineering Aspects 263, 3-3 (2005).

Vollhardt, D.: Effect of interfacial molecular recognition of non-surface-active species on the main characteristics of monolayers. Adv. Colloid Interface Sci. 116, 63-80 (2005).

Vollhardt, D., Fainerman, V. B. and Liu, F.: Thermodynamic and structural characterization of amphiphilic melamine-type monolayers. Journal of Physical Chemistry B 109, 11706-11711 (2005).

Vollhardt, D., Liu, F. and Rudert, R.: Molecular recognition of dissolved pyrimidine derivatives by a dialkyl melamine-type monolayer. Chemphyschem 6, 1246-1250 (2005).

Vollhardt, D., Liu, F. and Rudert, R.: The role of non-surface-active species at interfacial molecular recognition by melamine-type monolayers. Journal of Physical Chemistry B 109, 17635-17643 (2005).

Vollhardt, D., Liu, F., Rudert, R. and He, W.: Interfacial molecular recognition of dissolved thymine by medium chain dialkyl melamine-type monolayers. Journal of Physical Chemistry B 109, 10849-10857 (2005).

Vysotsky, Y. B., Bryantsev, V. S., Boldyreva, F. L., Fainerman, V. B. and Vollhardt, D.: Quantum chemical semiempirical approach to the structural and thermodynamic characteristics of fluoroalkanols at the air/water interface. Journal of Physical Chemistry B 109, 454-462 (2005).

Wang, D. Y., Duan, H. W. and Möhwald, H.: The water/oil interface: the emerging horizon for self-assembly of nanoparticles. Soft Matter 1, 412-416 (2005).

Wang, X. L., Zheng, S. P., He, Q., Brezesinski, G., Möhwald, H. and Li, J. B.: Hydrolysis reaction analysis of L-alpha-distearoylphosphatidyleholine monolayer catalyzed by phospholipase A(2) with polarization-modulated infrared reflection absorption spectroscopy. Langmuir 21, 1051-1054 (2005).

Wantke, K. D., Ortegren, J., Fruhner, H., Andersen, A. and Motschmann, H.: The influence of the sublayer on the surface dilatational modulus. Colloids and Surfaces A-Physicochemical and Engineering Aspects 261, 75-83 (2005).

Wojciechowski, K., Buffle, J. and Miller, R.: The synergistic adsorption of fatty acid and azacrown ether at the toluene-water interface. Colloids and Surfaces A-Physicochemical and Engineering Aspects 261, 49-55 (2005).

Zbytovska, J., Kiselev, M. A., Funari, S. S., Garamus, V. M., Wartewig, S. and Neubert, R.: Influence of phytosphingosine-type ceramides on the structure of DMPC membrane. Chem. Phys. Lipids 138, 69-80 (2005).

Zebli, B., Susha, A. S., Sukhorukov, G. B., Rogach, A. L. and Parak, W. J.: Magnetic targeting and cellular uptake of polymer microcapsules simultaneously functionalized with magnetic and luminescent nanocrystals. Langmuir 21, 4262-4265 (2005).

Zhai, X. H., Bartel, M., Brezesinski, G., Rattay, B., Möhwald, H. and Li, J. B.: Small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) studies of amide phospholipid. Chem. Phys. Lipids 133, 79-88 (2005).

Zhai, X. H., Brezesinski, G., Möhwald, H. and Li, J. B.: Impact of inhibiting activity of indole inhibitors on phospholipid hydrolysis by phospholipase A(2). Colloids and Surfaces A-Physicochemical and Engineering Aspects 256, 51-55 (2005).

Zhang, G., Wang, D. Y., Gu, Z. Z., Hartmann, J. and Möhwald, H.: Two-dimensional non-close-packing arrays derived from self-assembly of biomineralized hydrogel spheres and their patterning applications. Chem. Mater. 17, 5268-5274 (2005).

Zhang, G., Wang, D. Y., Gu, Z. Z. and Möhwald, H.: Fabrication of superhydrophobic surfaces from binary colloidal assembly. Langmuir 21, 9143-9148 (2005).

Zhang, G., Wang, D. Y. and Möhwald, H.: Decoration of microspheres with gold nanodots-giving colloidal spheres valences. Angewandte Chemie-International Edition 44, 7767-7770 (2005).

Zhang, G., Wang, D. Y. and Möhwald, H.: Patterning microsphere surfaces by templating colloidal crystals. Nano Letters 5, 143-146 (2005).

Zhang, H., Wang, C. L., Li, M. J., Ji, X. L., Zhang, J. H. and Yang, B.: Fluorescent nanocrystal-polymer composites from aqueous nanocrystals: Methods without ligand exchange. Chem. Mater. 17, 4783-4788 (2005).

Zhou, Y.: Recent advances in ionic liquids for synthesis of inorganic nanomaterials. Current Nanoscience 1, 35-42 (2005).

Patents 2005:

Dr. Dirk G. Kurth, Dr. Iles Alexander -Intern. Center Verfahren zur Temperaturmessung in einem mikrofluidik Kanal einer Mikrofluidikvorrichtung (2005).

Prof. Dr. Helmuth Möhwald, Heidemarie Zastrow, Hansjoachim Stechemesser, Dr. Heinz Lichtenfeld Verfahren zur Veränderung der Stabilität von wässrigen Dispersionen (2005).

Interfaces 2006

Aksenenko, E. V., Kovalchuk, V. I., Fainerman, V. B. and Miller, R.: Surface dilational rheology of mixed adsorption layers at liquid interfaces. Adv. Colloid Interface Sci. 122, 57-66 (2006).

An, Z. H., Möhwald, H. and Li, J. B.: pH controlled permeability of lipid/protein biomimetic microcapsules. Biomacromolecules 7, 580-585 (2006).

Andersen, A., Oertegren, J., Koelsch, P., Wantke, D. and Motschmann, H.: Oscillating bubble SHG on surface elastic and surface viscoelastic systems: New insights in the dynamics of adsorption layers. Journal of Physical Chemistry B 110, 18466-18472 (2006).

Andreeva, D. V., Gorin, D. A., Shchukin, D. G. and Sukhorukov, G. B.: Magnetic microcapsules with low permeable polypyrrole skin layer. Macromolecular Rapid Communications 27, 931-936 (2006).

Biesheuvel, P. M., Lindhoud, S., Stuart, M. A. C. and de Vries, R.: Phase behavior of mixtures of oppositely charged protein nanoparticles at asymmetric charge ratios. Physical Review E 73, Art. No. 041408 (2006).

Biesheuvel, P. M., Mauser, T., Sukhorukov, G. B. and Möhwald, H.: Micromechanical theory for pH-dependent polyelectrolyte multilayer capsule swelling. Macromolecules 39, 8480-8486 (2006).

Bondarenko, M. P., Zholkovskiy, E. K., Kovalchuk, V. I. and Vollhardt, D.: Distributions of ionic concentrations and electric field around the three-phase contact at high rates of Langmuir-Blodgett deposition. Journal of Physical Chemistry B 110, 1843-1855 (2006).

Brahler, M., Georgieva, R., Buske, N., Müller, A., Müller, S., Pinkernelle, J., Teichgräber, U., Voigt, A. and Bäumler, H.: Magnetite-loaded carrier erythrocytes as contrast agents for magnetic resonance imaging. Nano Letters 6, 2505-2509 (2006).

Bukreeva, T. V., Parakhonsky, B. V., Skirtach, A. G., Susha, A. S. and Sukhorukov, G. B.: Preparation of polyelectrolyte microcapsules with silver and gold nanoparticles in a shell and the remote destruction of microcapsules under laser irradiation. Crystallography Reports 51, 863-869 (2006).

Carriere, D., Dubois, M., Schönhoff, M., Zemb, T. and Möhwald, H.: Counter-ion activity and microstructure in polyelectrolyte complexes as determined by osmotic pressure measurements. Physical Chemistry Chemical Physics 8, 3141-3146 (2006).

Corvis, Y., Barzyk, W., Brezesinski, G., Mrabet, N., Badis, M., Hecht, S. and Rogalska, E.: Interactions of a fungistatic antibiotic, griseofulvin, with phospholipid monolayers used as models of biological membranes. Langmuir 22, 7701-7711 (2006).

Corvis, Y., Brezesinski, G., Rink, R., Walcarius, A., Van der Heyden, A., Mutelet, F. and Rogalska, E.: Analytical investigation of the interactions between SC3 hydrophobin and lipid layers: Elaborating of nanostructured matrixes for immobilizing redox systems. Anal. Chem. 78, 4850-4864 (2006).

De Geest, B. G., Vandenbroucke, R. E., Guenther, A. M., Sukhorukov, G. B., Hennink, W. E., Sanders, N. N., Demeester, J. and De Smedt, S. C.: Intracellularly degradable polyelectrolyte microcapsules. Advanced Materials 18, 1005-1009 (2006).

De Geest, B.G., Déjugnat, C., Verhoeven, E., Sukhorukov, G.B., Jonas, A.M., Plain, J., Demeester J., De Smedt S.C.: Layer-by-layer coating of degradable microgels for pulsed drug delivery. Journal of Controlled Release, 116 (2), 159-169. (2006).

Delorme, N., Dubois, M., Garnier, S., Laschewsky, A., Weinkamer, R., Zemb, T. and Fery, A.: Surface immobilization and mechanical properties of catanionic hollow faceted polyhedrons. Journal of Physical Chemistry B 110, 1752-1758 (2006).

Delorme, N. and Fery, A.: Direct method to study membrane rigidity of small vesicles based on atomic force microscope force spectroscopy. Physical Review E 74, Art. No. 030901 (2006).

Dong, W. F., Wang, R. M., Mao, G. Z. and Möhwald, H.: Self-assembled molecular patterns of fatty acid on graphite in the presence of metal ions. Soft Matter 2, 686-692 (2006).

Dubois, M., Schönhoff, M., Meister, A., Belloni, L., Zemb, T. and Möhwald, H.: Equation of state of colloids coated by polyelectrolyte multilayers. Physical Review E 74, Art. No. 051402 (2006).
Elsner, N., Kozlovskaya, V., Sukhishvili, S. A. and Fery, A.: pH-Triggered softening of crosslinked hydrogen-bonded capsules. Soft Matter 2, 966-972 (2006).

Fainerman, V. B., Kovalchuk, V. I., Lucassen-Reynders, E. H., Grigoriev, D. O., Ferri, J. K., Leser, M. E., Michel, M., Miller, R. and Möhwald, H.: Surface-pressure isotherms of monolayers formed by microsize and nanosize particles. Langmuir 22, 1701-1705 (2006).

Fainerman, V. B., Lylyk, S. V., Ferri, J. K., Miller, R., Watzke, H., Leser, M. E. and Michel, M.: Adsorption kinetics of proteins at the solution/air interfaces with controlled bulk convection. Colloids and Surfaces A-Physicochemical and Engineering Aspects 282, 217-221 (2006).

Fainerman, V. B., Miller, R., Ferri, J. K., Watzke, H., Leser, M. E. and Michel, M.: Reversibility and irreversibility of adsorption of surfactants and proteins at liquid interfaces. Adv. Colloid Interface Sci. 123, 163-171 (2006).

Fainerman, V. B., Mys, V. D., Makievski, A. V. and Miller, R.: Application of the maximum bubble pressure technique for dynamic surface tension studies of surfactant solutions using the Sugden two-capillary method. J. Colloid Interface Sci. 304, 222-225 (2006).

Fainerman, V. B., Mys, V. D., Makievski, A. V., Petkov, J. T. and Miller, R.: Dynamic surface tension of micellar solutions in the millisecond and submillisecond time range. J. Colloid Interface Sci. 302, 40-46 (2006).

Fainerman, V. B. and Vollhardt, D.: Surface pressure isotherm for the fluid state of Langmuir monolayers. Journal of Physical Chemistry B 110, 10436-10440 (2006).

Fainerman, V. B. and Vollhardt, D.: Reply to "comments on the thermodynamic justification of an equation of state for monolayers" by Anatoly I. Rusanov. Journal of Physical Chemistry B 110, 3448-3448 (2006).

Ferri, J. K., Dong, W. F., Miller, R. and Möhwald, H.: Elastic moduli of asymmetric ultrathin free-standing polyelectrolyte nanocomposites. Macromolecules 39, 1532-1537 (2006).

Fery, A.: Micro-mechanics and adhesion of artificial capsules. From method-development to understanding structure-property relations. Potsdam 2006.

Fery, A.: Intelligent microcapsules. Nachrichten aus der Chemie 54, 854-857 (2006).

Gao, C. Y., Chen, B. and Möhwald, H.: Thermosensitive poly(allylamine)-g-poly(N-isopropylacrylamide) copolymers: Salt-tuned phase separation, particle formation and their applicability on curved surface. Colloids and Surfaces A-Physicochemical and Engineering Aspects 272, 203-210 (2006).

Ge, L. Q., Möhwald, H. and Li, J. B.: Mechanical property of lipid-coated polyelectrolyte microcapsules. Journal of Nanoscience and Nanotechnology 6, 2489-2493 (2006).

Germain, M., Balaguer, P., Nicolas, J. C., Lopez, F., Esteve, J. P., Sukhorukov, G. B., Winterhalter, M., Richard-Foy, H. and Fournier, D.: Protection of mammalian cell used in biosensors by coating with a polyelectrolyte shell. Biosensors & Bioelectronics 21, 1566-1573 (2006).

Gorin, D. A., Shchukin, D. G., Mikhailov, A. I., Köhler, K., Sergeev, S. A., Portnov, S. A., Taranov, I. V., Kislov, V. V. and Sukhorukov, G. B.: Effect of microwave radiation on polymer microcapsules containing inorganic nanoparticles. Technical Physics Letters 32, 70-72 (2006).

Grigoriev, D. O., Leser, M. E., Michel, M. and Miller, R.: Component separation in spread sodium stearoyl lactylate (SSL) monolayers induced by high surface pressure. Colloids and Surfaces A-Physicochemical and Engineering Aspects 286, 57-61 (2006).

Gromelski, S. and Brezesinski, G.: DNA condensation and interaction with Zwitterionic phospholipids mediated by divalent cations. Langmuir 22, 6293-6301 (2006).

Higuchi, M., Kurth, D. G. and Yamamoto, K.: Functional modules: Metal ion assembly in novel topological poly(phenylazomethine)s. Thin Solid Films 499, 234-241 (2006).

Iyota, H., Krastev, R. and Müller, H. J.: Thermodynamic studies on thin liquid films. III: Miscibility in adsorbed films at film interfaces (vol 283, pg 975, 2005). Colloid Polym. Sci. 284, 455-457 (2006).

Javier, A. M., Kreft, O., Alberola, A. P., Kirchner, C., Zebli, B., Susha, A. S., Horn, E., Kempter, S., Skirtach, A. G., Rogach, A. L., Radler, J., Sukhorukov, G., Benoit, M. and Parak, W. J.: Combined atomic force microscopy and optical microscopy measurements as a method to investigate particle uptake by cells. Small 2, 394-400 (2006).

Köhler, K., Biesheuvel, P. M., Weinkamer, R., Möhwald, H. and Sukhorukov, G. B.: Salt-induced swelling-to-shrinking transition in polyelectrolyte multilayer capsules. Phys. Rev. Lett. 97, Art. No. 188301 (2006).

Köhler, K., Möhwald, H. and Sukhorukov, G. B.: Thermal behavior of polyelectrolyte multilayer microcapsules: 2. Insight into molecular mechanisms for the PDADMAC/PSS system. Journal of Physical Chemistry B 110, 24002-24010 (2006).

Kolb, U., Buscher, K., Helm, C. A., Lindner, A., Thünemann, A. F., Menzel, M., Higuchi, M. and Kurth, D. G.: The solid-state architecture of a metallosupramolecular polyelectrolyte. Proc. Natl. Acad. Sci. U. S. A. 103, 10202-10206 (2006).

Kovalchuk, N. M. and Vollhardt, D.: Marangoni instability and spontaneous non-linear oscillations produced at liquid interfaces by surfactant transfer. Adv. Colloid Interface Sci. 120, 1-31 (2006).

Kovalchuk, N. M. and Vollhardt, D.: Spontaneous nonlinear oscillation produced by alcohol transfer through water/alkane interface: An experimental study. Colloids and Surfaces A-Physicochemical and Engineering Aspects 291, 101-109 (2006).

Kovalchuk, N. M. and Vollhardt, D.: Surfactant transfer through a liquid membrane: Origin of spontaneous oscillations at the membrane/acceptor phase interface. Journal of Physical Chemistry B 110, 9774-9778 (2006).

Kreft, O., Georgieva, R., Bäumler, H., Steup, M., Müller-Röber, B., Sukhorukov, G. B. and Möhwald, H.: Red blood cell templated polyelectrolyte capsules: A novel vehicle for the stable encapsulation of DNA and proteins. Macromolecular Rapid Communications 27, 435-440 (2006).

Kuang, M., Wang, D. Y. and Möhwald, H.: Fabrication of Au@$CaCO_3$ nanoparticles by in situ mineralization in hydrogel microspheres. Chem. Mater. 18, 1073-1075 (2006).

Kuhnhenn, V., Krägel, J., Horstmann, U. and Miller, R.: Surface shear rheological studies of marine Phytoplankton cultures - Nitzschia closterium, Thalassiosira rotula, Thalassiosira punctigera and Phaeocystis sp. Colloids and Surfaces B-Biointerfaces 47, 29-35 (2006).

Kurth, D. G. and Higuchi, M.: Transition metal ions: weak links for strong polymers. Soft Matter 2, 915-927 (2006).

Laschewsky, A., Mertoglu, M., Kubowicz, S. and Thünemann, A. F.: Lamellar structured nanoparticles formed by complexes of a cationic block copolymer and perfluorodecanoic acid. Macromolecules 39, 9337-9345 (2006).

Li, X. F., Hao, X. F., Xu, D., Zhang, G., Zhong, S. L., Na, H. and Wang, D. Y.: Fabrication of sulfonated poly(ether ether ketone ketone) membranes with high proton conductivity. J. Membr. Sci. 281, 1-6 (2006).

Liu, S. Q., Möhwald, H., Volkmer, D. and Kurth, D. G.: Polyoxometalate-based electro- and photochromic dual-mode devices. Langmuir 22, 1949-1951 (2006).

Liz, C. C. C., Petkova, V., Benattar, J. J., Michel, M., Leser, M. E. and Miller, R.: X-ray reflectivity studies of liquid films stabilized by mixed beta-lactoglobulin - Acacia gum systems. Colloids and Surfaces A-Physicochemical and Engineering Aspects 282, 109-117 (2006).

Lu, C. H., Dönch, I., Nolte, M. and Fery, A.: Au nanoparticle-based multilayer ultrathin films with covalently linked nanostructures: Spraying layer-by-layer assembly and mechanical property characterization. Chem. Mater. 18, 6204-6210 (2006).

Lutz, J. F., Pfeifer, S., Chanana, M., Thünemann, A. F. and Bienert, R.: H-bonding-directed self-assembly of synthetic copolymers containing nucleobases: Organization and colloidal fusion in a noncompetitive solvent. Langmuir 22, 7411-7415 (2006).

Ma, Y. J., Dong, W. F., Hempenius, M. A., Möhwald, H. and Vancso, G. J.: Redox-controlled molecular permeability of composite-wall microcapsules. Nature Materials 5, 724-729 (2006).

Maltseva, E., Shapovalov, V. L., Möhwald, H. and Brezesinski, G.: Ionization state and structure of L-1,2-dipalmitoylphosphatidylglycerol monolayers at the liquid/air interface. Journal of Physical Chemistry B 110, 919-926 (2006).

Mauser, T., Dejugnat, C., Möhwald, H. and Sukhorukov, G. B.: Microcapsules made of weak polyelectrolytes: Templating and stimuli-responsive properties. Langmuir 22, 5888-5893 (2006).

Mauser, T., Dejugnat, C. and Sukhorukov, G. B.: Balance of hydrophobic and electrostatic forces in the pH response of weak polyelectrolyte capsules. Journal of Physical Chemistry B 110, 20246-20253 (2006).

Mishra, N. C., Müller, H. J., Möhwald, H. and Krastev, R.: Interactions and stability of foam films from pentaethyleneglycol monodecyl ether. Colloids and Surfaces A-Physicochemical and Engineering Aspects 282, 92-98 (2006).

Mishra, N. C., Müller, H. J., Möhwald, H. and Krastev, R.: Properties of foam films stabilized with tetraethylammonium perfluorooctane-sulfonate. J. Fluorine Chem. 127, 133-139 (2006).

Muruganathan, R. M., Krastev, R., Müller, H. J. and Möhwald, H.: Foam films stabilized with dodecyl maltoside. 2. Film stability and gas permeability. Langmuir 22, 7981-7985 (2006).

Nakanishi, T., Miyashita, N., Michinobu, T., Wakayama, Y., Tsuruoka, T., Ariga, K. and Kurth, D. G.: Perfectly straight nanowires of fullerenes bearing long alkyl chains on graphite. Journal of the American Chemical Society 128, 6328-6329 (2006).

Nolte, M., Dönch, I. and Fery, A.: Freestanding polyelectrolyte films as sensors for osmotic pressure. Chemphyschem 7, 1985-1989 (2006).

Nolte, M. and Fery, A.: Freestanding polyelectrolyte multilayers as functional and construction elements. IEE Proceedings-Nanobiotechnology 153, 112-120 (2006).

Noskov, B. A., Lin, S. Y., Loglio, G., Rubio, R. G. and Miller, R.: Dilational viscoelasticity of PEO-PPO-PEO triblock copolymer films at the air-water interface in the range of high surface pressures. Langmuir 22, 2647-2652 (2006).

Noskov, B. A., Loglio, G., Lin, S. Y. and Miller, R.: Dynamic surface elasticity of polyelectrolyte/surfactant adsorption films at the air/water interface: Dodecyltrimethylammonium bromide and copolymer of sodium 2-acrylamido-2-methyl-1-propansulfonate with N-isopropylacrylamide. J. Colloid Interface Sci. 301, 386-394 (2006).

Petrov, J. G., Andreeva, T. D. and Möhwald, H.: Fluorination of the hydrophilic head accelerates the collapse of the monolayer but stabilizes the bilayer of a long-chain trifluoroethyl ether on water. Langmuir 22, 4136-4143 (2006).

Pilakowska-Pietras, D., Lunkenheimer, K. and Piasecki, A.: Investigations on foamability of surface-chemically pure aqueous solutions of functionalized alkylaldonamides. J. Colloid Interface Sci. 294, 423-428 (2006).

Prevot, M., Déjugnat, C., Möhwald, H., Sukhorukov, G.B.: Behavior of Temperature-Sensitive PNIPAM Confined in Polyelectrolyte Capsules. ChemPhysChem, 7 (12), 2497-2502 (2006).

Qu, D., Pedersen, J. S., Garnier, S., Laschewsky, A., Möhwald, H. and von Klitzing, R.: Effect of polymer charge and geometrical confinement on ion distribution and the structuring in semidilute polyelectrolyte solutions: Comparison between AFM and SAXS. Macromolecules 39, 7364-7371 (2006).

Raichur, A. M., Voros, J., Textor, M. and Fery, A.: Adhesion of polyelectrolyte microcapsules through biotin-streptavidin specific interaction. Biomacromolecules 7, 2331-2336 (2006).

Reincke, F., Kegel, W. K., Zhang, H., Nolte, M., Wang, D. Y., Vanmaekelbergh, D. and Möhwald, H.: Understanding the self-assembly of charged nanoparticles at the water/oil interface. Physical Chemistry Chemical Physics 8, 3828-3835 (2006).

Rusu, M., Kuckling, D., Möhwald, H. and Schönhoff, M.: Adsorption of novel thermosensitive graft-copolymers: Core-shell particles prepared by polyelectrolyte multilayer self-assembly. J. Colloid Interface Sci. 298, 124-131 (2006).

Rusu, M., Wohlrab, S., Kuckling, D., Möhwald, H. and Schönhoff, M.: Coil-to-globule transition of PNIPAM graft copolymers with charged side chains: A 1H and 2H NMR and spin relaxation study. Macromolecules 39, 7358-7363 (2006).

Sadasivan, S., Köhler, K. and Sukhorukov, G. B.: Fabrication of organized porphyrin-nanotube-attached heat-sensitive polyelectrolyte capsules. Advanced Functional Materials 16, 2083-2088 (2006).

Sadasivan, S. and Sukhorukov, G. B.: Fabrication of hollow multifunctional spheres containing MCM-41 nanoparticles and magnetite nanoparticles using layer-by-layer method. J. Colloid Interface Sci. 304, 437-441 (2006).

Sanz, A., Nogales, A., Ezquerra, T. A., Lotti, N., Munari, A. and Funari, S. S.: Order and segmental mobility during polymer crystallization: Poly (butylene isophthalate). Polymer 47, 1281-1290 (2006).

Schoeler, B., Delorme, N., Doench, I., Sukhorukov, G. B., Fery, A. and Glinel, K.: Polyelectrolyte films based on polysaccharides of different conformations: Effects on multilayer structure and mechanical properties. Biomacromolecules 7, 2065-2071 (2006).

Sczech, R. and Riegler, H.: Molecularly smooth cellulose surfaces for adhesion studies. J. Colloid Interface Sci. 301, 376-385 (2006).

Shapovalov, V. L. and Brezesinski, G.: Breakdown of the Gouy-Chapman model for highly charged Langmuir monolayers: Counterion size effect. Journal of Physical Chemistry B 110, 10032-10040 (2006).

Shchukin, D. G., Gorin, D. A. and Möhwald, H.: Ultrasonically induced opening of polyelectrolyte microcontainers. Langmuir 22, 7400-7404 (2006).

Shchukin, D. G., Köhler, K. and Möhwald, H.: Microcontainers with electrochemically reversible permeability. Journal of the American Chemical Society 128, 4560-4561 (2006).

Shchukin, D. G. and Möhwald, H.: Sonochemical nanosynthesis at the engineered interface of a cavitation microbubble. Physical Chemistry Chemical Physics 8, 3496-3506 (2006).

Shchukin, D. G. and Sviridov, D. V.: Photocatalytic processes in spatially confined micro- and nanoreactors. Journal of Photochemistry and Photobiology C-Photochemistry Reviews 7, 23-39 (2006).

Shchukin, D. G., Zheludkevich, M. and Möhwald, H.: Feedback active coatings based on incorporated nanocontainers. J. Mater. Chem. 16, 4561-4566 (2006).

Shchukin, D. G., Zheludkevich, M., Yasakau, K., Lamaka, S., Ferreira, M. G. S. and Möhwald, H.: Layer-by-layer assembled nanocontainers for self-healing corrosion protection. Advanced Materials 18, 1672-1678 (2006).

Skirtach, A. G., Javier, A. M., Kreft, O., Köhler, K., Alberola, A. P., Möhwald, H., Parak, W. J. and Sukhorukov, G. B.: Laser-induced release of encapsulated materials inside living cells. Angewandte Chemie-International Edition 45, 4612-4617 (2006).

Stein, E. W., Volodkin, D. V., McShane, M. J. and Sukhorukov, G. B.: Real-time assessment of spatial and temporal coupled catalysis within polyelectrolyte microcapsules containing coimmobilized mucose oxiase and peroxidase. Biomacromolecules 7, 710-719 (2006).

Teixeira, C. V., Blanzat, M., Koetz, J., Rico-Lattes, I. and Brezesinski, G.: In-plane miscibility and mixed bilayer microstructure in mixtures of catanionic glycolipids and zwitterionic phospholipids. Biochimica et Biophysica Acta-Biomembranes 1758, 1797-1808 (2006).

Thirumoorthy, K., Nandi, N. and Vollhardt, D.: Prediction of the handedness of the domains of monolayers of D-N-palmitoyl aspartic acid: Integrated molecular orbital and molecular mechanics based calculation. Colloids and Surfaces A-Physicochemical and Engineering Aspects 282, 222-226 (2006).

Thirumoorthy, K., Nandi, N., Vollhardt, D. and Oliveira, O. N.: Semiempirical quantum mechanical calculations of dipolar interaction between dipyridamole and dipalmitoyl phosphatidyl choline in Langmuir monolayers. Langmuir 22, 5398-5402 (2006).

Thünemann, A. F., Kubowicz, S., von Berlepsch, H. and Möhwald, H.: Two-compartment micellar assemblies obtained via aqueous self-organization of synthetic polymer building blocks. Langmuir 22, 2506-2510 (2006).

Thünemann, A. F., Kurth, D. G., Beinhoff, M., Bienert, R. and Schulz, B.: V-shaped crystalline structures of di-n-alkyl esters of phosphoric acid. Langmuir 22, 5856-5861 (2006).

Thünemann, A. F., Schütt, D., Kaufner, L., Pison, U. and Möhwald, H.: Maghemite nanoparticles protectively coated with poly(ethylene imine) and poly(ethylene oxide)-block-poly(glutamic acid). Langmuir 22, 2351-2357 (2006).

Thünemann, A. F., Schütt, D., Sachse, R., Schlaad, H. and Möhwald, H.: Complexes of poly(ethylene oxide)-block-poly(L-glutamate) and diminazene. Langmuir 22, 2323-2328 (2006).

Tong, W. J., Gao, C. Y. and Möhwald, H.: Stable weak polyelectrolyte microcapsules with pH-responsive permeability. Macromolecules 39, 335-340 (2006).

Tong, W. J., Song, H. Q., Gao, C. Y. and Möhwald, H.: Equilibrium distribution of permeants in polyelectrolyte microcapsules filled with negatively charged polyelectrolyte: The influence of ionic strength and solvent polarity. Journal of Physical Chemistry B 110, 12905-12909 (2006).

Twardos, M., Dennin, M. and Brezesinski, G.: Characterization of anomalous flow and phase behavior in a Langmuir monolayer of 2-hydroxytetracosanoic acid. Journal of Physical Chemistry B 110, 22245-22250 (2006).

Vodouhe, C., Le Guen, E., Garza, J. M., Francius, G., Dejugnat, C., Ogier, J., Schaaf, P., Voegel, J. C. and Lavalle, P.: Control of drug accessibility on functional polyelectrolyte multilayer films. Biomaterials 27, 4149-4156 (2006).

Vollhardt, D.: Nucleation in monolayers. Adv. Colloid Interface Sci. 123, 173-188 (2006).

Vollhardt, D. and Wagner, R.: Effect of the exchange of substituent position in an amide amphiphile on the monolayer characteristics. Journal of Physical Chemistry B 110, 14881-14889 (2006).

Vysotsky, Y. B., Muratov, D. V., Boldyreva, F. L., Fainerman, V. B., Vollhardt, D. and Miller, R.: Quantum chemical analysis of the thermodynamics of 2D cluster formation of n-carboxylic acids at the air/water interface. Journal of Physical Chemistry B 110, 4717-4730 (2006).

Wang, B., Chen, K., Jiang, S., Reincke, F., Tong, W. J., Wang, D. Y. and Gao, C. Y.: Chitosan-mediated synthesis of gold nanoparticles on patterned poly(dimethylsiloxane) surfaces. Biomacromolecules 7, 1203-1209 (2006).

Wang, D. Y.: Marriage of ATRP and nanoparticles: Happy end and fresh start. Abstracts of Papers of the American Chemical Society 231, 138-PMSE (2006).

Wang, J., Wang, D. Y., Sobal, N. S., Giersig, M., Jiang, M. and Möhwald, H.: Stepwise directing of nanocrystals to self-assemble at water/oil interfaces. Angewandte Chemie-International Edition 45, 7963-7966 (2006).

Publications/Department of Interfaces

Weidinger, I. M., Murgida, D. H., Dong, W. F., Möhwald, H. and Hildebrandt, P.: Redox processes of cytochrome c immobilized on solid supported polyelectrolyte multilayers. Journal of Physical Chemistry B 110, 522-529 (2006).

Weiss, S. I., Sieverling, N., Niclasen, M., Maucksch, C., Thünemann, A. F., Möhwald, H., Reinhardt, D., Rosenecker, J. and Rudolph, C.: Uronic acids functionalized polyethyleneimine (PEI)-polyethyleneglycol (PEG)-graft-copolymers as novel synthetic gene carriers. Biomaterials 27, 2302-2312 (2006).

Wojciechowski, K., Grigoriev, D., Ferdani, R. and Gokel, G. W.: Mixed monolayers of alkylated aza-crown ethers and palmitic acid at the air-water surface. Langmuir 22, 8409-8415 (2006).

Yue, X. L., Dobner, B., Iimura, K., Kato, T., Möhwald, H. and Brezesinski, G.: Weak first-order tilting transition in monolayers of mono- and bipolar docosanol derivatives. Journal of Physical Chemistry B 110, 22237-22244 (2006).

Zhang, G., Wang, D. Y. and Möhwald, H.: Nanoembossment of Au patterns on microspheres. Chem. Mater. 18, 3985-3992 (2006).

Zhang, H., Edwards, E. W., Wang, D. Y. and Möhwald, H.: Directing the self-assembly of nanocrystals beyond colloidal crystallization. Physical Chemistry Chemical Physics 8, 3288-3299 (2006).

Zhang, H., Wang, D. Y. and Möhwald, H.: Ligand-selective aqueous synthesis of one-dimensional CdTe nanostructures. Angewandte Chemie-International Edition 45, 748-751 (2006).

Zhang, H., Wang, D. Y., Yang, B. and Möhwald, H.: Manipulation of aqueous growth of CdTe nanocrystals to fabricate colloidally stable one-dimensional nanostructures. Journal of the American Chemical Society 128, 10171-10180 (2006).

Zhang, X. M., He, Q., Cui, Y., Duan, L. and Li, J. B.: Human serum albumin supported lipid patterns for the targeted recognition of microspheres coated by membrane based on ss-DNA hybridization. Biochem. Biophys. Res. Commun. 349, 920-924 (2006).

Patents 2006:

Dmitry Shchukin, Helmuth Möhwald, Mikhail Zheludkevich, Mario G. S. Ferreira
Container-based pigments for active corrosion protection with self-healing effect (2006).

Theory & Bio-Systems 2005

Asfaw, M.: Adhesion of multi-component membranes and strings. Potsdam 2005.

Bastolla, U., Lässig, M., Manrubia, S. C. and Valleriani, A.: Biodiversity in model ecosystems, I: coexistence conditions for competing species. J. Theor. Biol. 235, 521-530 (2005).

Bastolla, U., Lässig, M., Manrubia, S. C. and Valleriani, A.: Biodiversity in model ecosystems, II: species assembly and food web structure. J. Theor. Biol. 235, 531-539 (2005).

Bischofs, I. B. and Schwarz, U. S.: Effect of poisson ratio on cellular structure formation. Phys. Rev. Lett. 95, Art. No. 068102 (2005).

Breidenich, M., Netz, R. R. and Lipowsky, R.: The influence of non-anchored polymers on the curvature of vesicles. Mol. Phys. 103, 3169-3183 (2005).

Brinkmann, M., Kierfeld, J. and Lipowsky, R.: Stability of liquid channels or filaments in the presence of line tension. Journal of Physics-Condensed Matter 17, 2349-2364 (2005).

Georgieva, R., Dimova, R., Sukhorukov, G., Ibarz, G. and Möhwald, H.: Influence of different salts on micro-sized polyelectrolyte hollow capsules. J. Mater. Chem. 15, 4301-4310 (2005).

Gruhn, T. and Lipowsky, R.: Temperature dependence of vesicle adhesion. Physical Review E 71, Art. No. 011903 (2005).

Haluska, C., Marchi-Artzner, V., Brienne, J., Lehn, J. M., Lipowsky, R. and Dimova, R.: Fusion of functionalized giant vesicles. Biophys. J. 88, 66A-66A (2005).

Illya, G., Lipowsky, R. and Shillcock, J. C.: Effect of chain length and asymmetry on material properties of bilayer membranes. J. Chem. Phys. 122, Art. No. 244901 (2005).

Imparato, A., Shillcock, J. C. and Lipowsky, R.: Shape fluctuations and elastic properties of two-component bilayer membranes. Europhys. Lett. 69, 650-656 (2005).

Kierfeld, J., Kühne, T. and Lipowsky, R.: Discontinuous unbinding transitions of filament bundles. Phys. Rev. Lett. 95, Art. No. 038102 (2005).

Kierfeld, J. and Lipowsky, R.: Duality mapping and unbinding transitions of semiflexible and directed polymers. Journal of Physics A-Mathematical and General 38, L155-L161 (2005).

Kierfeld, J. and Vinokur, V. M.: Competitive localization of vortex lines and interacting bosons. Phys. Rev. Lett. 94, Art. No. 077005 (2005).

Klumpp, S. and Lipowsky, R.: Active diffusion of motor particles. Phys. Rev. Lett. 95, Art. No. 268102 (2005).

Klumpp, S. and Lipowsky, R.: Cooperative cargo transport by several molecular motors. Proc. Natl. Acad. Sci. U. S. A. 102, 17284-17289 (2005).

Klumpp, S., Nieuwenhuizen, T. M. and Lipowsky, R.: Self-organized density patterns of molecular motors in arrays of cytoskeletal filaments. Biophys. J. 88, 3118-3132 (2005).

Klumpp, S., Nieuwenhuizen, T. M. and Lipowsky, R.: Movements of molecular motors: Ratchets, random walks and traffic phenomena. Physica E-Low-Dimensional Systems & Nanostructures 29, 380-389 (2005).

Kraikivski, P., Lipowsky, R. and Kierfeld, J.: Activated dynamics of semiflexible polymers on structured substrates. European Physical Journal E 16, 319-340 (2005).

Kraikivski, P., Lipowsky, R. and Kierfeld, J.: Point force manipulation and activated dynamics of polymers adsorbed on structured substrates. Europhys. Lett. 71, 138-144 (2005).

Kumar, N. A. and Seidel, C.: Polyelectrolyte brushes with added salt. Macromolecules 38, 9341-9350 (2005).

Linke, G. T., Lipowsky, R. and Gruhn, T.: Free fluid vesicles are not exactly spherical. Physical Review E 71, Art. No. 051602 (2005).

Lipowsky, R., Brinkmann, M., Dimova, R., Franke, T., Kierfeld, J. and Zhang, X. Z.: Droplets, bubbles, and vesicles at chemically structured surfaces. Journal of Physics-Condensed Matter 17, S537-S558 (2005).

Lipowsky, R., Brinkmann, M., Dimova, R., Haluska, C., Kierfeld, J. and Shillcock, J.: Wetting, budding, and fusion-morphological transitions of soft surfaces. Journal of Physics-Condensed Matter 17, S2885-S2902 (2005).

Lipowsky, R. and Klumpp, S.: 'Life is motion': multiscale motility of molecular motors. Physica A-Statistical Mechanics and Its Applications 352, 53-112 (2005).

Merlo, C., Dill, K. A. and Weikl, T. R.: phi values in protein-folding kinetics have energetic and structural components. Proc. Natl. Acad. Sci. U. S. A. 102, 10171-10175 (2005).

Merlo, C. and Weikl, T. R.: The structural interpretation of phi-values in protein folding kinetics. Biophys. J. 88, 213A-213A (2005).

Müller, M. J. I., Klumpp, S. and Lipowsky, R.: Molecular motor traffic in a half-open tube. Journal of Physics-Condensed Matter 17, S3839-S3850 (2005).

Navas, B. P., Lohner, K., Deutsch, G., Sevcsik, S., Riske, K. A., Dimova, R., Garidel, P. and Pabst, G.: Composition dependence of vesicle morphology and mixing properties in a bacterial model membrane system. Biochimica et Biophysica Acta-Biomembranes 1716, 40-48 (2005).

Nieuwenhuizen, T. M., Klumpp, S. and Lipowsky, R.: Walks of molecular motors interacting with immobilized filaments. Physica A-Statistical Mechanics and Its Applications 350, 122-130 (2005).

Nikolov, V. Y. and Dimova, R. I.: Binding of avidin to biotinylated membranes: Isothermal titrational calorimetry study. Biophys. J. 88, 581A-581A (2005).

Ortiz, V., Nielsen, S. O., Discher, D. E., Klein, M. L., Lipowsky, R. and Shillcock, J.: Dissipative particle dynamics simulations of polymersomes. Biophys. J. 88, 243A-243A (2005).

Ortiz, V., Nielsen, S. O., Discher, D. E., Klein, M. L., Lipowsky, R. and Shillcock, J.: Dissipative particle dynamics simulations of polymersomes. Journal of Physical Chemistry B 109, 17708-17714 (2005).

Richter, A., Pleimling, M. and Hüller, A.: Density of states of classical spin systems with continuous degrees of freedom. Physical Review E 71, Art. No. 056705 (2005).

Riske, K. A. and Dimova, R.: Electro-deformation and poration of giant vesicles viewed with high temporal resolution. Biophys. J. 88, 1143-1155 (2005).

Riske, K. A. and Dimova, R.: Timescales involved in electro-deformation, poration and fusion of giant vesicles resolved with fast digital imaging. Biophys. J. 88, 241A-241A (2005).

Safran, S. A., Gov, N., Nicolas, A., Schwarz, U. S. and Tlusty, T.: Physics of cell elasticity, shape and adhesion. Physica a-Statistical Mechanics and Its Applications 352, 171-201 (2005).

Schwarz, U. S. and Bischofs, I. B.: Physical determinants of cell organization in soft media. Medical Engineering & Physics 27, 763-772 (2005).

Seemann, R., Brinkmann, M., Kramer, E. J., Lange, F. F. and Lipowsky, R.: Wetting morphologies at microstructured surfaces. Proc. Natl. Acad. Sci. U. S. A. 102, 1848-1852 (2005).

Shillcock, J. C. and Lipowsky, R.: Tension-induced fusion of bilayer membranes and vesicles. Nature Materials 4, 225-228 (2005).

Tielborger, K. and Valleriani, A.: Can seeds predict their future? Germination strategies of density-regulated desert annuals. Oikos 111, 235-244 (2005).

Valleriani, A.: Algebraic determination of the evolutionary stable germination fraction. Theoretical Population Biology 68, 197-203 (2005).

Weikl, T. R.: Loop-closure events during protein folding: Rationalizing the shape of Phi-value distributions. Proteins-Structure Function and Bioinformatics 60, 701-711 (2005).

Zhou, H. J.: Long-range frustration in finite connectivity spin glasses: a mean-field theory and its application to the random K-satisfiability problem. New Journal of Physics 7, Art. No. 123 (2005).

Zhou, H. J.: Long-range frustration in a spin-glass model of the vertex-cover problem. Phys. Rev. Lett. 94, Art. No. 217203 (2005).

Zhou, H. J. and Lipowsky, R.: Dynamic pattern evolution on scale-free networks. Proc. Natl. Acad. Sci. U. S. A. 102, 10052-10057 (2005).

Zhou, H. J. and Zhang, Y.: Hierarchical chain model of spider capture silk elasticity. Phys. Rev. Lett. 94, Art. No. 028104 (2005).

Theory & Bio-Systems 2006

Abada, A., Bouakaz, K. and Azi, O.: Infrared behaviour of high-temperature quantum chromodynamics (QCD). Phys. Scr. 74, 77-103 (2006).

Asfaw, M., Rozycki, B., Lipowsky, R. and Weikl, T. R.: Membrane adhesion via competing receptor/ligand bonds. Europhys. Lett. 76, 703-709 (2006).

Bischofs, I. B. and Schwarz, U. S.: Collective effects in cellular structure formation mediated by compliant environments: A Monte Carlo study. Acta Biomaterialia 2, 253-265 (2006).

Blecua, P., Lipowsky, R. and Kierfeld, J.: Line tension effects for liquid droplets on circular surface domains. Langmuir 22, 11041-11059 (2006).

Chelakkot, R., Lipowsky, R. and Gruhn, T.: Novel low-density structure for hard rods with adhesive end groups. Macromolecules 39, 7138-7143 (2006).

Dimova, R., Aranda, S., Bezlyepkina, N., Nikolov, V., Riske, K. A. and Lipowsky, R.: A practical guide to giant vesicles. Probing the membrane nanoregime via optical microscopy. Journal of Physics-Condensed Matter 18, S1151-S1176 (2006).

Dixit, P. D. and Weikl, T. R.: A simple measure of native-state topology and chain connectivity predicts the folding rates of two-state proteins with and without crosslinks. Proteins: Structure, Function, and Bioinformatics 64, 193-197 (2006).

Franke, T., Lipowsky, R. and Helfrich, W.: Adhesion of lipid membranes induced by CrCl3. Europhys. Lett. 76, 339-345 (2006).

Haluska, C. K., Riske, K. A., Marchi-Artzner, V., Lehn, J. M., Lipowsky, R. and Dimova, R.: Time scales of membrane fusion revealed by direct imaging of vesicle fusion with high temporal resolution. Proc. Natl. Acad. Sci. U. S. A. 103, 15841-15846 (2006).

Iber, D. and Gruhn, T.: Organisation of B-cell receptors on the cell membrane. IEE Proceedings Systems Biology 153, 401-404 (2006).

Illya, G., Lipowsky, R. and Shillcock, J. C.: Two-component membrane material properties and domain formation from dissipative particle dynamics. J. Chem. Phys. 125, Art. No. 114710 (2006).

Kierfeld, J.: Strings and filaments: from vortices to biopolymers. Potsdam 2006.

Kierfeld, J.: Force-induced desorption and unzipping of semiflexible polymers. Phys. Rev. Lett. 97, Art. No. 058302 (2006).

Kierfeld, J. and Vinokur, V. M.: Slow crack propagation in heterogeneous materials. Phys. Rev. Lett. 96, Art. No. 175502 (2006).

Knecht, V., Mark, A. E. and Marrink, S. J.: Phase behavior of a phospholipid/fatty acid/water mixture studied in atomic detail. Journal of the American Chemical Society 128, 2030-2034 (2006).

Korn, C. and Schwarz, U. S.: Efficiency of initiating cell adhesion in hydrodynamic flow. Phys. Rev. Lett. 97, Art. No. 138103 (2006).

Kraikivski, P., Lipowsky, R. and Kierfeld, J.: Enhanced ordering of interacting filaments by molecular motors. Phys. Rev. Lett. 96, Art. No. 258103 (2006).

Kraikivski, P., Pouligny, B. and Dimova, R.: Implementing both short- and long-working-distance optical trappings into a commercial microscope. Rev. Sci. Instrum. 77, Art. No. 113703 (2006).

Linke, G. T., Lipowsky, R. and Gruhn, T.: Osmotically induced passage of vesicles through narrow pores. Europhys. Lett. 74, 916-922 (2006).

Lipowsky, R., Chai, Y., Klumpp, S., Liepelt, S. and Müller, M. J. I.: Molecular motor traffic: From biological nanomachines to macroscopic transport. Physica A-Statistical Mechanics and its Applications 372, 34-51 (2006).

Naji, A., Seidel, C. and Netz, R. R.: Theoretical approaches to neutral and charged polymer brushes. Advances in Polymer Science 198, 149-183 (2006).

Reich, L. and Weikl, T. R.: Substructural cooperativity and parallel versus sequential events during protein unfolding. Proteins: Structure, Function, and Bioinformatics 63, 1052-1058 (2006).

Richter, A. and Gruhn, T.: Structure formation and fractionation in systems of polydisperse attractive rods. J. Chem. Phys. 125, Art. No. 064908 (2006).

Riske, K. A. and Dimova, R.: Electric pulses induce cylindrical deformations on giant vesicles in salt solutions. Biophys. J. 91, 1778-1786 (2006).

Rozycki, B., Lipowsky, R. and Weikl, T. R.: Adhesion of membranes with active stickers. Phys. Rev. Lett. 96, Art. No. 048101 (2006).

Rozycki, B., Weikl, T. R. and Lipowsky, R.: Adhesion of membranes via switchable molecules. Physical Review E 73, Art. No. 061908 (2006).

Schwarz, U. S., Erdmann, T. and Bischofs, I. B.: Focal adhesions as mechanosensors: The two-spring model. Biosystems 83, 225-232 (2006).

Sharif, M. H.: High performance computing of $1/x$ & e^{+x} in alpha, intel, and opteron processors. Duisburg 2006.

Shillcock, J. C. and Lipowsky, R.: The computational route from bilayer membranes to vesicle fusion. Journal of Physics-Condensed Matter 18, S1191-S1219 (2006).

Sinn, C. G., Antonietti, M. and Dimova, R.: Binding of calcium to phosphatidylcholine-phosphatidylserine membranes. Colloids and Surfaces A-Physicochemical and Engineering Aspects 282, 410-419 (2006).

Valleriani, A.: Evolutionarily stable germination strategies with time-correlated yield. Theoretical Population Biology 70, 255-261 (2006).

Valleriani, A. and Tielborger, K.: Effect of age on germination of dormant seeds. Theoretical Population Biology 70, 1-9 (2006).

Imprint

Publisher: Max Planck Institute of Colloids and Interfaces

Address: Wissenschaftspark Golm, Am Mühlenberg 1, 14476 Potsdam

Phone: +49 (0) 331/567-7814

Fax: +49 (0) 331/567-7875

E-mail: info@mpikg.mpg.de

Internet: www.mpikg.mpg.de

Editorial: Katja Schulze

Design and Illustration: Stefan Pigur, www.pigurdesign.de

Printed by: Druckhaus Berlin-Mitte GmbH

Potsdam, June 2007