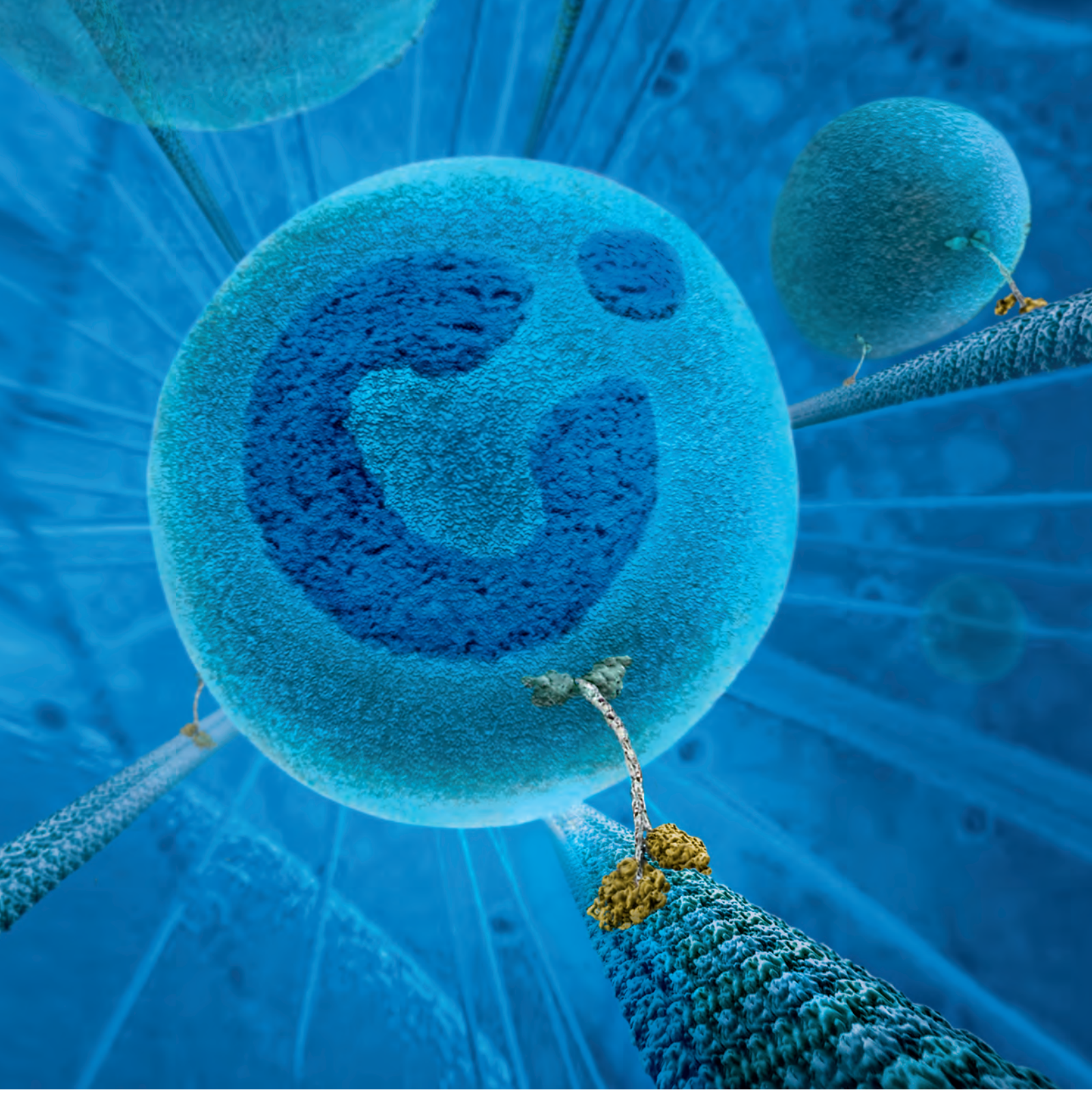
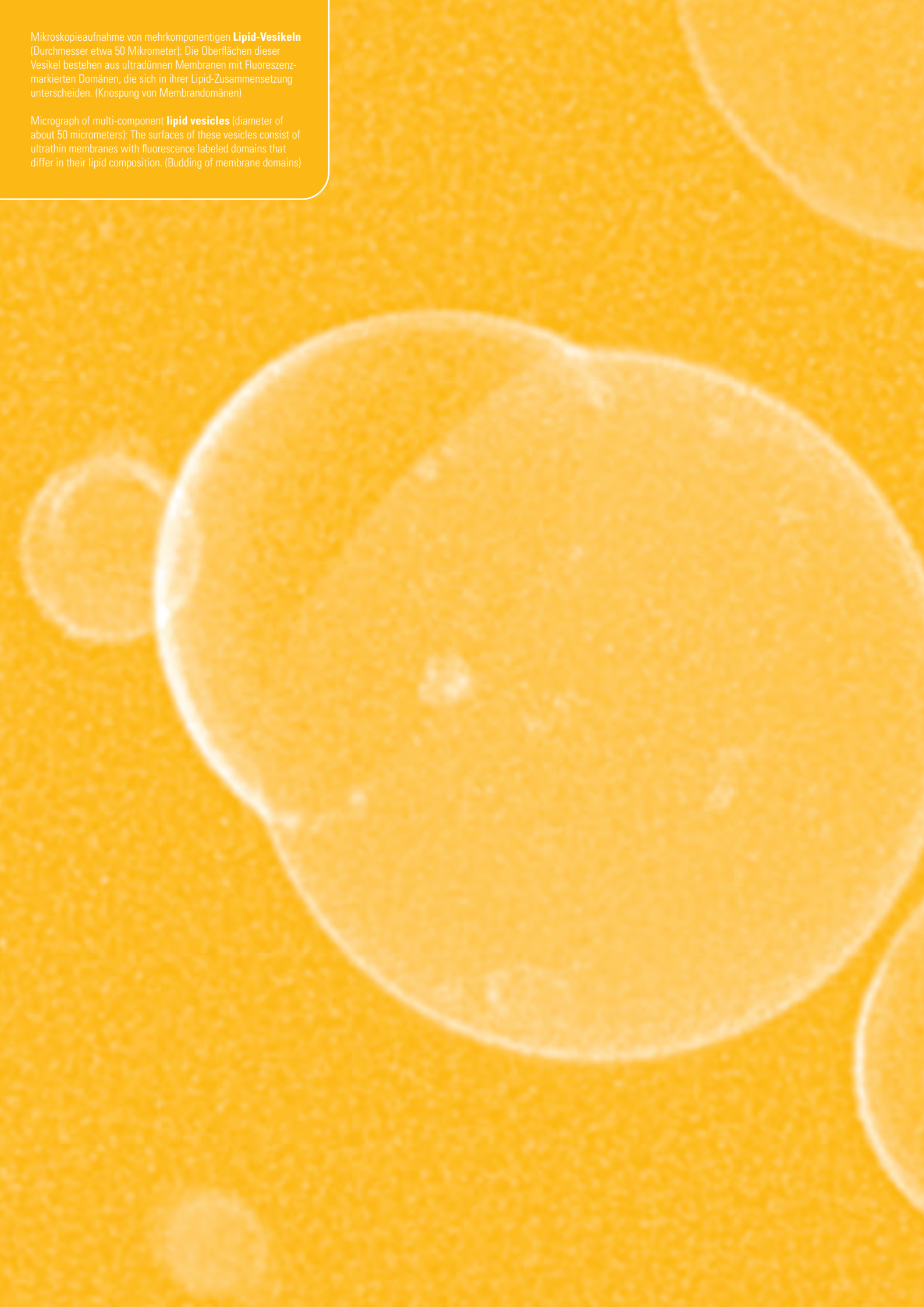


Max Planck Institute of Colloids and Interfaces

REPORT 2007-2008

MAX-PLANCK-GESELLSCHAFT



Mikroskopieaufnahme von mehrkomponentigen **Lipid-Vesikeln** (Durchmesser etwa 50 Mikrometer): Die Oberflächen dieser Vesikel bestehen aus ultradünnen Membranen mit Fluoreszenz-markierten Domänen, die sich in ihrer Lipid-Zusammensetzung unterscheiden. (Knospung von Membrandomänen)

Micrograph of multi-component **lipid vesicles** (diameter of about 50 micrometers): The surfaces of these vesicles consist of ultrathin membranes with fluorescence labeled domains that differ in their lipid composition. (Budding of membrane domains)

Max Planck Institute of Colloids and Interfaces

REPORT 2007-2008

Imprint
Publisher: Max Planck Institute of Colloids and Interfaces
Address: Science Park Potsdam-Golm, Am Mühlenberg 1, 14476 Potsdam
Phone: +49 (0) 331/567-7814
Fax: +49 (0) 331/567-7875
Email: info@mpikg.mpg.de
Internet: www.mpikg.mpg.de
Editorial: Katja Schulze
Design and Illustration: www.pigurdesign.de
Printed by: Druckhaus Berlin-Mitte GmbH
Potsdam, June 2009

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„Aus winzigen Keimen entsteht Gewaltiges.
[Ex minimis seminibus nascuntur ingentia.]"
Lucius Seneca

„Aus kleinen Dingen kann groß' Sach' entspringen."
Holländisches Sprichwort

Dieser Bericht beschreibt die Aktivitäten des Max-Planck-Instituts für Kolloid- und Grenzflächenforschung (MPI-KG), das 1992 als eines der ersten Max-Planck-Institute in den neuen Bundesländern gegründet wurde und seit 1999 im Wissenschaftspark Potsdam-Golm, angesiedelt ist. Das MPI-KG besteht zurzeit aus fünf Abteilungen und mehreren Servicegruppen, wobei die neu eingerichtete Abteilung „Biomolekulare Systeme" (Peter Seeberger) bis zur Fertigstellung unseres Erweiterungsgebäudes an der Freien Universität Berlin untergebracht ist.

Dieses Vorwort gibt zunächst eine kurze Einführung in das Forschungsgebiet des MPI-KG und einen Überblick über die aktuellen Schwerpunkte der einzelnen Abteilungen. Dabei soll auch deutlich werden, dass die Forschungsaktivitäten aller fünf Abteilungen eng miteinander verknüpft sind.

Die Kolloid- und Grenzflächenforschung beschäftigt sich mit sehr kleinen bzw. ultradünnen Strukturen im Nano- und Mikrometerbereich. Einerseits handelt es sich bei diesen Nanostrukturen um eine „Welt der versteckten Dimensionen", andererseits bestimmt die komplexe Architektur und Dynamik dieser Strukturen das Verhalten von sehr viel größeren Systemen wie biomimetischen Verbundmaterialien und biologischen Organismen.

Ein tieferes Verständnis von Kolloiden und Grenzflächen ist deshalb Voraussetzung für die Entwicklung von „intelligenten" Wirkstoffträgern und Biomaterialien. Dazu ist ein interdisziplinärer Zugang notwendig, der chemische Synthese und biomimetische Materialentwicklung mit physikalischer Charakterisierung und theoretischer Modellierung verknüpft.

Die Nano- und Mikrostrukturen, die am MPI-KG erforscht werden, sind aus noch kleineren, nämlich atomaren und molekularen Bausteinen aufgebaut. Es ist im Prinzip möglich, diese Bausteine mit Instrumenten wie dem Rasterkraftmikroskop zu greifen, aber diese „Greifarme" sind relativ unhandlich, so dass ein derartiger Zusammenbau selbst für eine einzelne Nanostruktur sehr aufwändig ist. Außerdem benötigt man für die weitere Forschung und Entwicklung viele Kopien der gleichen Struktur.

Die Synthese und der Zusammenbau der atomaren und molekularen Bausteine nutzt deshalb das Prinzip der Selbstorganisation aus: man stellt die äußeren Bedingungen so ein, dass sich die Bausteine „von selbst" miteinander verbinden und größere Strukturen aufbauen. Die beiden Abteilungen „Biomolekulare Systeme" (Peter Seeberger) und „Kolloidchemie" (Markus Antonietti) beschäftigen sich schwerpunktmäßig mit diesem Systemaufbau.

In der Abteilung „Biomolekulare Systeme", die im Jahr 2008 neu eingerichtet wurde, werden „maßgeschneiderte" Zuckermoleküle synthetisiert und mit anderen molekularen Gruppen verknüpft. Diese komplexen Kohlehydrate können andere Kohle-

Foto: Göran Gnaudschun

hydrate sowie Proteine und Antikörper an ihrem molekularen Aufbau erkennen und diskriminieren, ein Prozess, der mit Hilfe sogenannter Zuckerchips systematisch untersucht wird. Ein langfristiges Ziel ist dabei die Entwicklung von Impfstoffen auf Zuckerbasis.

Die Abteilung „Kolloidchemie" setzt verschiedenartige Makromoleküle ein, um daraus mesoskopische Verbundsysteme und Hybridmaterialien mit unterschiedlicher Architektur aufzubauen. Der Schwerpunkt liegt dabei auf der gezielten Kodierung von Strukturbildung und Selbstorganisation, d. h. die Moleküle enthalten bestimmte Muster, die die Strukturbildung steuern und die Zielstruktur weitgehend festlegen. Ein weiterer Schwerpunkt dieser Abteilung ist die Umwandlung von Biomasse in Kohle mittels der hydrothermalen Karbonisierung, ein Prozess, der einen wichtigen Beitrag zur Fixierung von CO_2 liefern könnte.

Weitere Nanostrukturen, die sich „von selbst" organisieren, sind molekulare Monoschichten sowie Multischichten aus positiv und negativ geladenen Polymeren, zwei Schwerpunkte der Abteilung „Grenzflächen" (Helmuth Möhwald). Die Nanostrukturen werden dabei an mesoskopischen und makroskopischen Grenzflächen „aufgehängt" und können dann mit physikalischen Untersuchungsmethoden sehr präzise vermessen werden. Die Multischichten von geladenen Polymeren lassen sich für die Verkapselung von ganz unterschiedlichen Wirkstoffen einsetzen und haben deshalb ein großes Anwendungspotential.

Nano- und Mikrostrukturen sind hierarchisch aufgebaut. Besonders eindrucksvolle Beispiele für diesen „verschachtelten" Systemaufbau finden sich in mineralisierten Geweben, wie Knochen, Zähnen oder Muschelschalen, sowie in Pflanzen und deren Zellwänden. Diese Systeme werden in der Abteilung „Biomaterialien" (Peter Fratzl) mit physikalischen Methoden erforscht. Dabei wird auch die Methode der fokussierten Synchrotronstrahlung eingesetzt, die es erlaubt, die Struktur von Mikrodomänen des Materials mit atomarer Auflösung sichtbar zu machen. Im Zentrum des Interesses stehen die Struktur-Funktions-Beziehungen dieser natürlichen Materialien, insbesondere ihre außergewöhnlichen mechanischen Eigenschaften, die sich ständig wechselnden äußeren Bedingungen anpassen.

Die Aktivitäten der vier experimentellen Abteilungen werden durch theoretische Untersuchungen in der Abteilung „Theorie & Bio-Systeme" (Reinhard Lipowsky) ergänzt. Aktuelle Schwerpunkte der Theorie sind molekulare Maschinen und mehrkomponentige Membranen. Zur Abteilung gehört auch ein Labor für die experimentelle Untersuchung von Lipid-Membranen und -Vesikeln. Diese theoretischen und experimentellen Aktivitäten verfolgen das langfristige Ziel, die grundlegenden Mechanismen und generellen Prinzipien aufzuklären, die die Selbstorganisation von Bio-Systemen im Nanobereich bestimmen.

Alle Forschungsgebiete, die hier erwähnt wurden, werden im Hauptteil dieses Berichts sehr viel genauer und detaillierter beschrieben. Dieser Hauptteil ist nach den fünf Abteilungen des Instituts gegliedert und setzt sich aus den Forschungsberichten der einzelnen Arbeitsgruppen zusammen.

Neben der intensiven Forschungstätigkeit hat das MPI-KG auch seine erfolgreiche Nachwuchsförderung weiter fortgesetzt. Inzwischen sind mehr als 40 ehemalige Mitarbeiter des MPI-KGs auf Professuren an Universitäten berufen worden.

Zum Schluss möchte ich zwei Ereignisse der beiden letzten Jahre besonders hervorheben, da sie die Entwicklung des MPI-KGs in den kommenden Jahren maßgeblich mitbestimmen werden. Erstens ist es uns gelungen, Peter Seeberger, vorher ETH Zürich, an das MPI-KG zu berufen. Zweitens hat die Leitung der Max-Planck-Gesellschaft unseren Antrag auf die Errichtung eines Erweiterungsgebäudes genehmigt. Die Notwendigkeit dieser Erweiterung ergibt sich auch aus der Zahl unserer Mitarbeiter, die in den vergangenen Jahren stetig gewachsen ist, vor allem durch die erfolgreiche Einwerbung von Drittmitteln.

An dieser Stelle möchte ich allen Kollegen und Mitarbeitern des MPI-KGs für ihre tatkräftige Unterstützung während der letzten beiden Jahre danken. Mein Dank gilt auch unserem wissenschaftlichen Beirat, der unsere Arbeit wieder sehr kompetent und konstruktiv begleitet hat, und nicht zuletzt der Leitung der Max-Planck-Gesellschaft für die nachhaltige Unterstützung bei der Berufung von Peter Seeberger und bei der Planung unseres Erweiterungsgebäudes.

Reinhard Lipowsky
Geschäftsführender Direktor 2007-2008

Preface

"Ex minimis seminibus nascuntur ingentia."
(Out of tiny things emerge gigantic ones)
Lucius Seneca

"Aus kleinen Dingen kann groß' Sach' entspringen."
Holländisches Sprichwort

This report describes the recent activities of the Max Planck Institute of Colloids and Interfaces (MPI-KG), which was founded in 1992 as one of the first new Max Planck Institutes after the reunification of Germany. The MPI-KG is located in the Science Park Potsdam-Golm and currently consists of five departments and several service groups. The new department on „Biomolecular Systems" (Peter Seeberger) is temporarily accommodated at the FU Berlin until the extension of our building has been completed.

This preface provides a brief introduction to some basic aspects of colloids and interfaces and a summary of the main research topics that are pursued in the different departments. The strong interconnections between all research activities within the MPI-KG will be emphasized.

Colloids and interfaces consist of very small and ultrathin structures with linear dimensions between nanometers and micrometers. On the one hand, the dynamics of these nanostructures involves relatively fast processes that evolve on the time scale of nanoseconds. These processes are difficult to study with direct imaging methods, and, thus, represent a „world of hidden dimensions". On the other hand, these small structures determine the properties and functions of much larger systems such as biomimetic materials and biological organisms.

A more systematic understanding of colloids and interfaces is a prerequisite for the development of „smart" drug delivery systems and biomaterials. Such a deeper understanding can only arise from an interdisciplinary approach that combines chemical synthesis and biomimetic materials science with physical analysis and characterization as well as theoretical modelling.

The nano- and microstructures that are investigated at the MPI-KG are built up from even smaller atomic and molecular building blocks. In principle, it is possible to hold and assemble these building blocks with special instruments such as the scanning force microscope. These „microhands" are, however, relatively thick and sticky, and such an assembly is very time-consuming even for an individual nanostructure. In addition, in order to characterize these structures and to develop them further, it is necessary to produce many copies or replicas of them.

Therefore, the synthesis and assembly of atomic and molecular building blocks is primarily based on self-assembly and self-organization. When placed into an appropriate environment, the building blocks assemble „by themselves" into well-defined larger structures. These structure formation processes represent the focus of the two departments on „Biomolecular Systems" (Peter Seeberger) and „Colloid Chemistry" (Markus Antonietti).

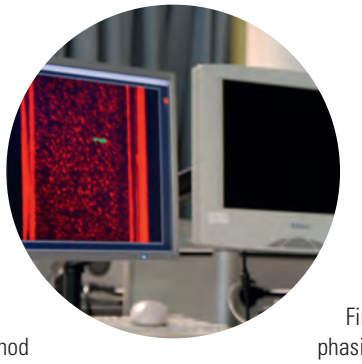
The department „Biomolecular Systems", which has been newly established in 2008, synthesizes and designs sugar molecules and carbohydrates with well-defined and fine-tuned architectures. These complex macromolecules are able to specifically recognize and distinguish other macromolecules such as proteins and antibodies, a process that is studied by immobilizing the molecules on so-called glycochips. A long-term goal of this research is to develop vaccines based on such sugar molecules.

In the department „Colloid Chemistry", a variety of macromolecules is used in order to construct mesoscopic compound systems and hybrid materials. One important aspect of this activity is the molecular encoding of self-assembly and self-organization by specific molecular groups that guide these processes towards a certain target structure. Another recent focus of the department is the transformation of biomass into coal using the process of hydrothermal carbonization. The latter process could provide an important contribution to carbon fixation and, thus, to the reduction of CO_2.

Additional nanostructures that arise via selforganization are monolayers of organic molecules and multilayers of positively and negatively charged polymers, two priorities of the department „Interfaces" (Helmuth Möhwald). These nanostructures are suspended at mesoscopic and macroscopic interfaces and, in this way, become accessible to a wide spectrum of imaging and scattering methods. The multilayers of polyelectrolytes can be used to encapsulate a variety of different molecules and nanoparticles with many promising applications in chemical engineering and pharmacology.

Nano- and microstructures are built up in a hierarchical fashion. Especially impressive examples for this „nested" system architecture are found in mineralized tissues such as bone, teeth, and seashells as well as in plants and their cell walls. These systems are studied in the department „Biomaterials" (Peter Fratzl) using a variety of ex-

Foto: Göran Ghaudschun



perimental characterization methods. One particularly powerful method is microfocussed synchrotron radiation, by which one can determine the structure of micrometer domains with atomic resolution and determine the structure-function relationships of these natural materials. One important aspect is their extraordinary mechanical properties, which can adapt to changing environmental conditions.

The activities of the four experimental departments are complemented by theoretical investigations in the department „Theory & Bio-Systems“ (Reinhard Lipowsky). Current priorities of this department are molecular machines as well as bio-membranes and vesicles that are also studied experimentally using optical microscopy. The long-term goal of these research activities is to elucidate the fundamental principles and generic mechanisms that govern the selforganization of biomimetic and biological systems in the nanoregime.

All research topics that have been mentioned here will be described in much more detail in the main body of this report, which is organized according to the five departments of the MPI-KG. Each department consists of several research groups, each of which will present its research results as obtained during the past two years.

Apart from its many research activities, the MPI-KG also continued its successful training of young scientists (in German: Nachwuchsförderung). Indeed, during the last 15 years, more than 40 alumni of the MPI-KG have taken up professorships in Germany and abroad.

Finally, I would like to emphasize two events during the past two years that will have a strong impact on the future development of our institute. First, Peter Seeberger, who has been at the ETH Zürich, has accepted our offer in 2008 and has now started to build up his new department. Second, our president has approved our proposal for an extension of our building. This extension reflects the steady growth of the MPI-KG during the last couple of years, primarily because we were quite successful in obtaining external funding.

I take this opportunity to thank all of my colleagues and associates at the MPI-KG for their active support during the past two years. It is also my pleasure to acknowledge the comprehensive advice that we again obtained from our scientific advisory board. Last not least, I am grateful to our president and to our vice-president for their continuous support of our institute.

Reinhard Lipowsky
Managing Director 2007-2008

Das Institut in Zahlen

Personal

Abb. 1 zeigt, dass das Stammpersonal, etwa 65 administrative und technische Mitarbeiter sowie 40 Wissenschaftler, über die Jahre konstant geblieben ist. Dagegen stieg die Zahl der meist jüngeren Wissenschaftler mit Anstellung über weniger als drei Jahre stetig auf etwa 200. Wenn man berücksichtigt, dass zusätzlich etwa 50 kurzzeitige Gäste im Institut arbeiten, wird klar, dass die Büros und Labors mit etwa 4000 m^2 Fläche überbelegt sind. Dennoch erwarten wir einen Anstieg der Mitarbeiterzahl mit dem Aufbau der Abteilung „Biomolekulare Systeme“, die zunächst auf dem Campus der Freien Universität Berlin untergebracht wird, ehe sie in den Erweiterungsbau des Instituts im Wissenschaftspark Potsdam-Golm umziehen kann.

Abb. 2 demonstriert, daß die Zahl der Doktoranden gerade 100 übersteigt, während die Zahl der Postdoktoranden über 70 angewachsen ist (**Abb. 3**). Während Postdoktoranden vorwiegend Ausländer sind, liegt deren Anteil bei den Doktoranden um 50%. Dieser Anteil ist wünschenswert und die Statistik zeigt auch, dass die Phase zu geringer deutscher Doktoranden Anfang des Jahrhunderts überwunden ist.

Unter den Wissenschaftlern sind Ausländer in der Mehrzahl, insgesamt liegt deren Anteil bei etwa 40%. Die Statistik der Herkunftsländer in **Abb. 4** zeigt, dass der Anteil der Europäer bei etwa 50% liegt, etwa zur Hälfte West- und Osteuropa. Ein weiteres Viertel sind chinesische Gäste.

Budget

Die institutionelle Förderung sank in den letzen Jahren stetig, und der Anstieg 2008 hat technische Gründe (**Abb. 5**). Die Max-Planck-Gesellschaft wurde weitgehend mehrwertsteuerpflichtig und dies wurde durch eine erhöhte Zuweisung aufgefangen. Dennoch erwarten wir mit der Einrichtung der fünften Abteilung einen erheblichen Etatzuwachs in den folgenden Jahren.

Fig. 1

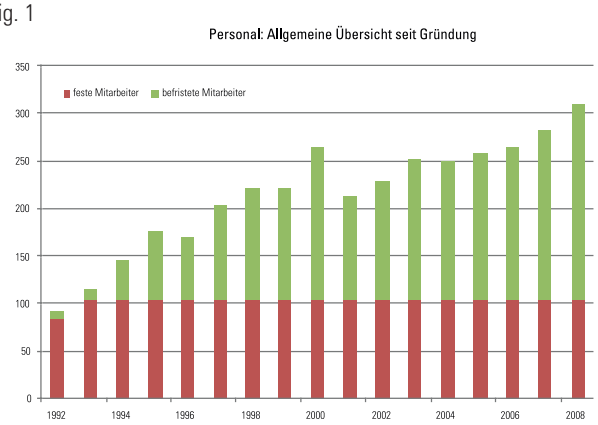


Fig. 3

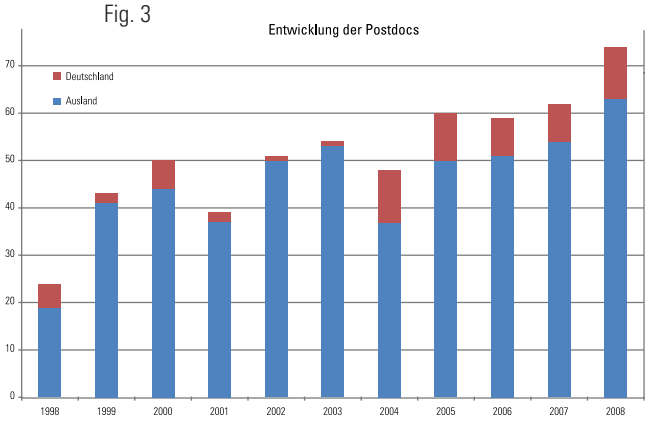


Fig. 2

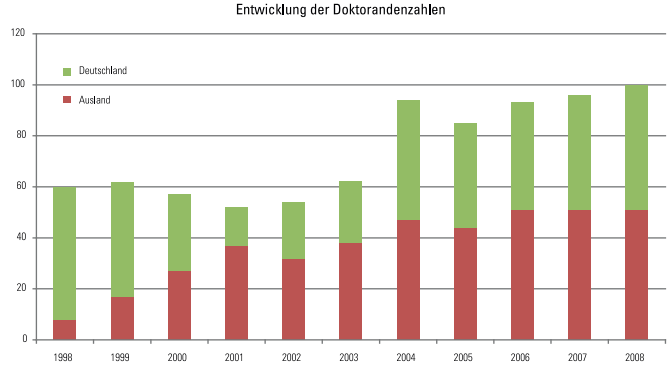
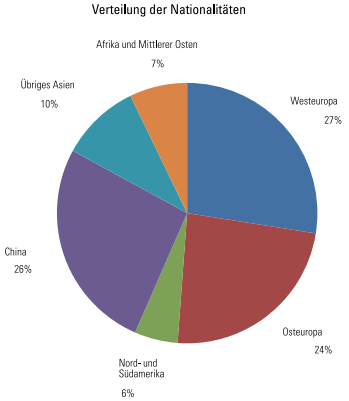


Fig. 4



Der Anteil der Drittmittelförderung liegt bei etwa 20% (**Abb. 6**). Insgesamt stieg er leicht an, es gibt aber erhebliche Schwankungen des Anteils einzelner Drittmittelgeber:

- Die EU-Förderung verringerte sich 2008 erstmals vor allem wegen des Übergangs vom 6. zum 7. Rahmenprogramm. Zudem haben viele Wissenschaftler, die EU-Mittel eingeworben haben, das Institut auf Professorenstellen verlassen und dorthin ihre Fördermittel übertragen.
- Trotz der Beschränkungen für Max-Planck-Wissenschaftler wuchs die Förderung durch die Deutsch Forschungsgemeinschaft (DFG), vor allem wegen der Gewährung einer Gemeinkostenpauschale.
- Die Förderung durch das Bundesministerium für Bildung und Forschung (BMBF), bei der Max-Planck-Forscher ebenfalls eingeschränkt sind, stieg an wegen einer besonderen Aktivität, dem NanoFutur-Preis von D. Shchukin.
- Die Industriemittel blieben konstant bei einem Anteil von 15% der Drittmittel. Dieser Anteil ist akzeptabel für ein Institut mit einem Grundlagenforschungsauftrag.

Wissenschaftliche Ergebnisse und deren Einfluss

Obwohl wir ein Forschungsinstitut und keine Universität sind, betrachten wir als wichtigsten Ertrag nicht Papier, sondern viele gut ausgebildete junge Wissenschafter. Es ist allerdings in der Wissenschaft zur Gewohnheit geworden, den Erfolg durch Publikationen und Zitationen zu messen, die vom „Institute for Scientific Information" (ISI) erfasst werden. Wie **Abb. 7a** zu entnehmen, haben die Zahlen der jährlichen Publikationen einen stabilen Wert oberhalb 300 erreicht. Der Anstieg internationaler Anerkennung wird auch sichtbar anhand des drastischen Anstiegs an Zitationen oberhalb 14.000 (**Abb. 7b**). Die Zahl übertrifft erheblich die entsprechenden viel größerer Institute, auch solcher mit älterer Geschichte, die von dem kumulativen Charakter der Zitationen profitieren. Diese Zahlen machen es auch verständlich, dass das Institut an der Spitze vieler Arten von Reihungen und Bewertungen liegt. Die letzte bemerkenswerte war das 2007 veröffentlichte „Forschungsrating Chemie" des Wissenschaftsrats, bei dem das Institut in Qualität und Effizienz den Spitzenplatz unter 77 Forschungsinstituten oder Fakultäten einnimmt.

Fig. 5

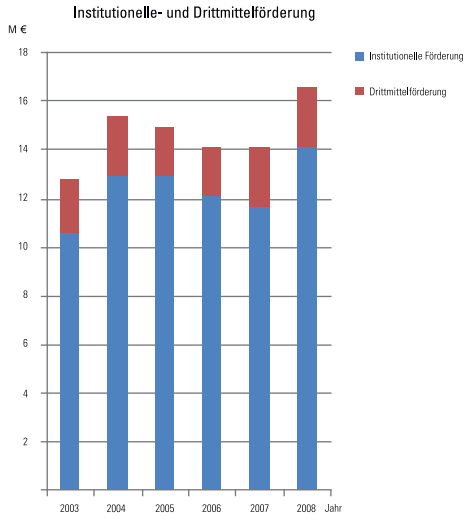


Fig. 6

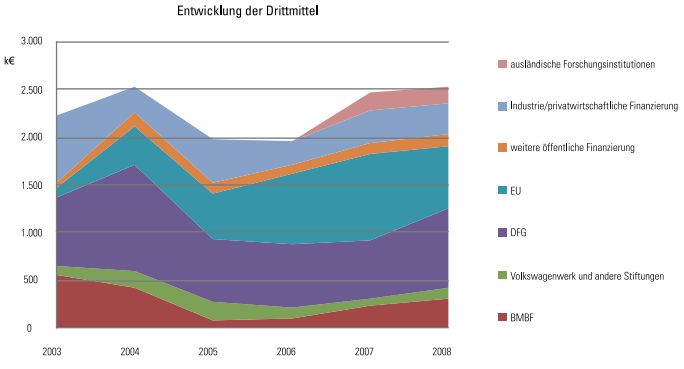


Fig. 7a

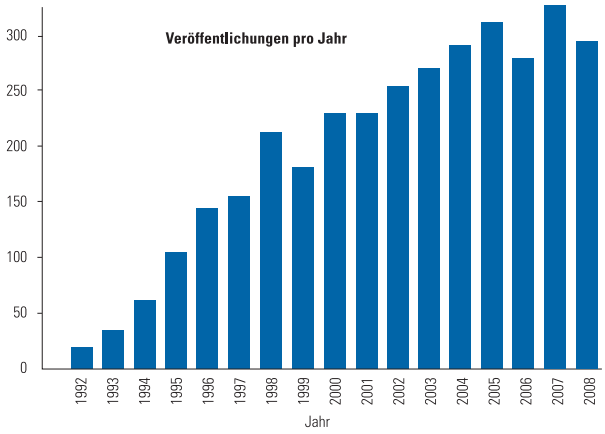
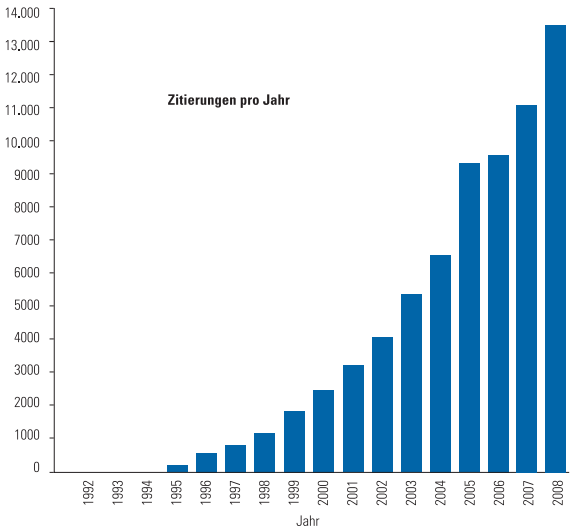


Fig. 7b



The Institute in Numbers

I. Personnel

Fig. 1 shows that staff, about 65 administrative and technical personnel and 40 scientists, has remained constant over many years. However, the number of scientists, mostly young ones with appointments for less than three years, has still been increasing towards close to 200. Taking into account that there are in addition about 50 short term guests in the institute the space of about 4000 m^2 is overcrowded. Still we expect an increase of the personnel with the set up of the department "Biomolecular Systems" which will be accommodated on the Campus of the Free University Berlin until it moves into the extension of the institute in the Sience Park Potsdam-Golm.

Fig. 2 demonstrates that the number of graduate students will exceed the amount of 100. That of postdocs is just increasing above 70 (**Fig. 3**). Whereas postdocs are mainly foreigners, for graduate students their fraction is near 50%. This is a desirable situation indicating that we have well overcome the shortage of German graduate students in the first years of this century.

Among scientists foreigners are the majority, in total their fraction is about 40%. Their origin by country is depicted in **Fig. 4**. The fraction of Europeans is about 50%, nearly equally divided between Eastern and Western Europe. Another quarter is taken up by Chinese guests.

Budget

The institutional funding has seen a steady decrease in the last years, and the increase in 2008 is for technical reasons (**Fig. 5**). There have been changes in the German tax law forcing the Max Planck society to pay sales tax, and this has been recovered by a budget increase. Still with the establishment of the 5th department we also anticipate a major budget increase in the years to come.

Fig. 1

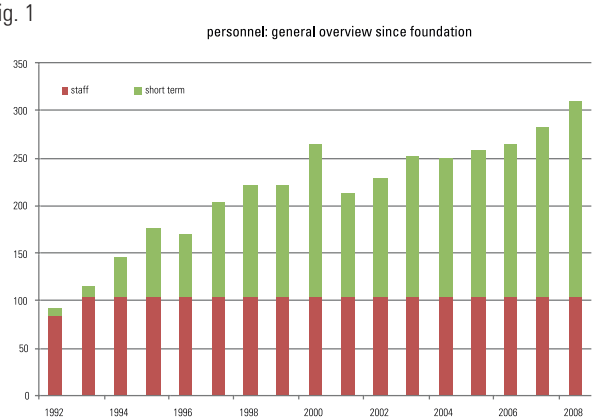


Fig. 3

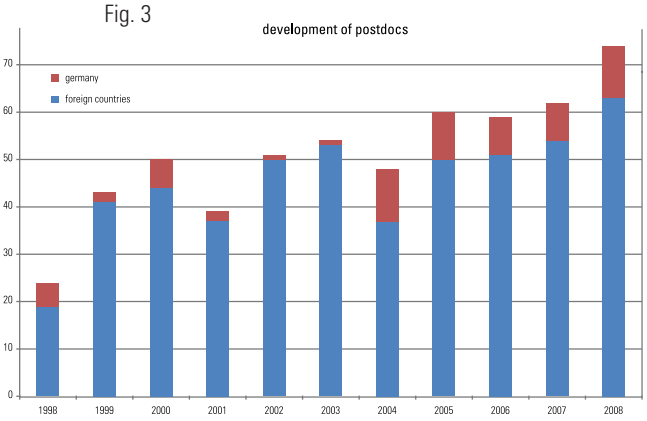


Fig. 2

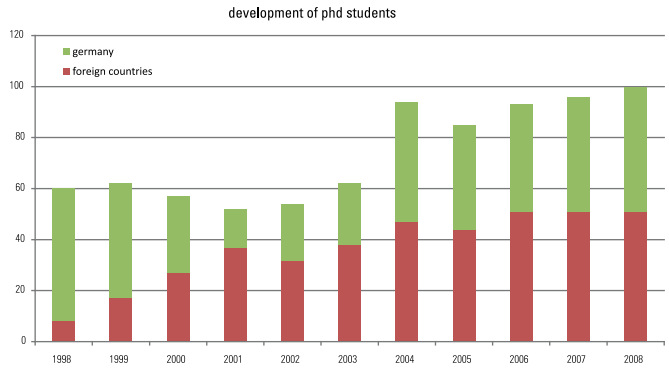
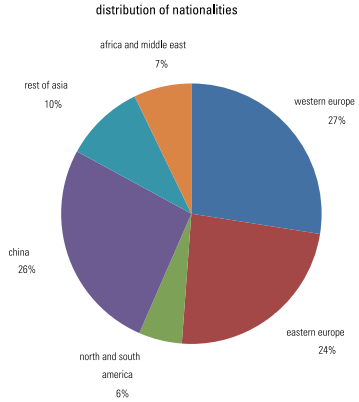


Fig. 4



External funding amounts to about 20% (**Fig. 6**). This overall has been slightly increasing but there have been considerable fluctuations concerning the different sources:

- EU funding has experienced the first decline in 2008 predominantly due to a change between the 6th and the 7th framework program. In addition many scientists who have been strong in EU funding have left on professor positions taking their funding with them.
- Despite its restriction for Max Planck scientists funding by the German Research Foundation (DFG) has increased, largely also due to introduction of overhead financing.
- Funding by the Ministry of Education and Research (BMBF), also restricted for Max Planck Institutes, has again increased, predominantly due to a special activity, the Nanofuture award for D. Shchukin.
- Industry funding has remained on a constant level of 15% of all funding. This is a reasonable level for an institute with a basic science mission.

Scientific Output and Impact

Although being a research institution, not a university, we consider the most important output not paper but the many well-trained young scientists leaving the institute. Yet it has become custom to measure success in science in publications and citations analyzed by the ISI. According to **Fig. 7a** the number of publications has reached a steady level above 300. The build-up of international reputation is also visible from the drastic increase in citations above 14.000 (**Fig. 7b**). This number much exceeds that of many large institutes, also those with a longer history that profit from the cumulative character of citations. These numbers make it also understandable that the institute ranks top in many types of rankings and ratings. The last notable has been the 2007 published chemistry research rating of the German Science Council which in quality and efficiency ranked our institute top among 77 research institutes or faculties.

Fig. 5

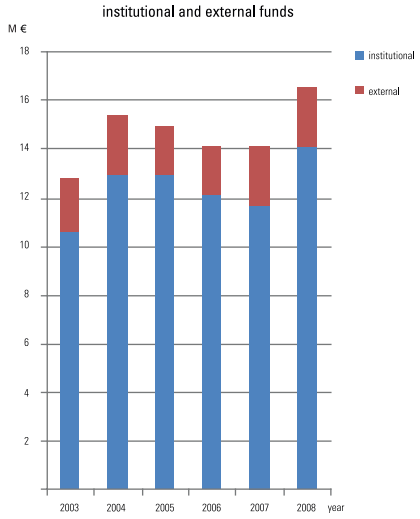


Fig. 6

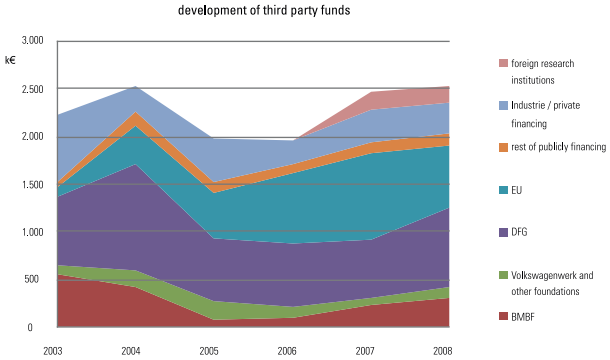


Fig. 7a

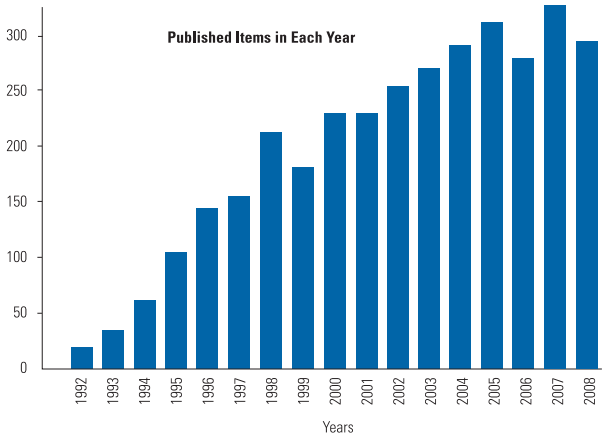
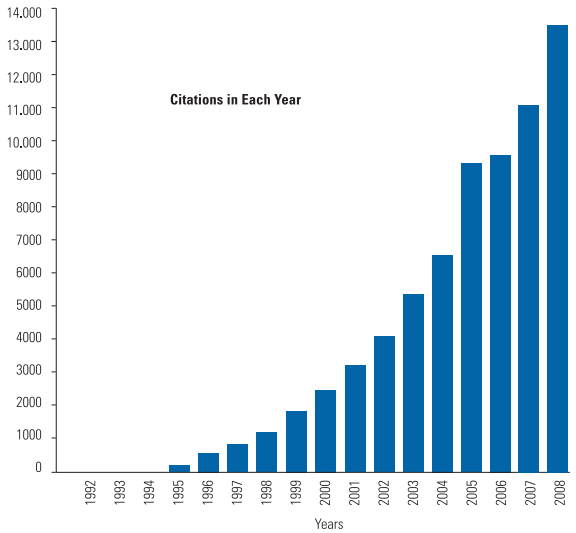


Fig. 7b



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

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 **Abb. 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.

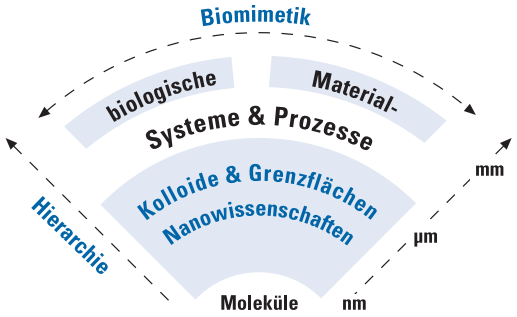


Abb. 1: Die Forschung am MPI-KG beschäftigt sich mit Strukturen und Prozessen, die zwischen dem Nano- und Mikrometerbereich liegen, d.h. mit dem traditionellen Bereich der Kolloid- und Grenzflächenforschung, der viele Ebenen, angefangen von Molekülen bis hin zu biomimetischen Materialien und biologischen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

Die Forschung am MPI für Kolloid- und Grenzflächenforschung basiert auf der Fachkenntnis von fünf 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 grenzflächengesteuerte 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 hydrophil 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 räumlichen 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. hydrophober Effekt) gesteuert. Die starke Abhängigkeit dieser Kräfte von Umgebungsparametern führt hin zu reaktiven und selbstheilenden Systemen.

Membranen und andere Grenzflächen können durch speziell hinzugefügte Moleküle und Partikel funktionalisiert werden. Am MPI-KG 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 MPI-KG 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 MPI-KG 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, Vesikeln aus Lipiden oder polymeren Doppelschichten aus Polyelektrolyt-

Multilagen bestehende Kapseln. In diesen Kompartimenten kann man physikalische und chemische Prozesse der Strukturbildung und Selbstorganisation 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 vom Marie-Curie Early Stage Training Netzwerk komplettiert wird, entscheidend gestärkt und unterstützt. Weitere Informationen über die Graduiertenprogramme finden Sie auf den folgenden Seiten.

Neu hinzugekommen ist die Abteilung „Biomolekulare Systeme“, die ab Januar 2009 unter Leitung von Prof. Dr. Peter H. Seeberger ihre Arbeit aufgenommen hat. Da dies außerhalb des Berichtzeitraums liegt, finden Sie hier kein gesondertes Kapitel dazu. Als aktueller Bestandteil des wissenschaftlichen Institutsprofils wird es dennoch einen einführenden Artikel geben, der die zukünftigen Entwicklungen und Erwartungen beschreibt.

Interfacing ist ein Schlüsselproblem bei der Anordnung von kontrollierten und funktionalen kolloidalen Superstrukturen. Dabei ist die Anlagerung von verschiedenen, speziell interagieren Bausteinen auf der Oberfläche zwingend notwendig. Sind Peptidsequenzen und deren komplett biologische Erkennung weit verbreitet und in vielen Variationen zu finden, fokussiert sich die Seeberger-Gruppe auf die Synthese von speziellen Zuckern und Mehrfachzuckern. Auf diese Weise soll die Erkennung und Wechselwirkung zwischen biologischen Systemen, aber auch bei Grenzflächen zwischen synthetischen Materialien und Biosystemen etabliert werden. Prof. Seeberger hat eine automatisierte Syntheseapparatur entwickelt, um Zuckermoleküle mit anderen Zuckern oder auch Molekülen zu verknüpfen. Damit hat er die Voraussetzungen für die Weiter- und Neuentwicklung von Zuckerbasierten Medikamenten und Impfstoffen geschaffen. Ein Beispiel ist das Impfen mit einem Glykolipid des Malaria-Parasiten oder die chemische Synthese von Heparin. Dieser Ansatz der Polysaccharidерkennung und -codierung ist einzigartig, auch für Kolloide und Grenzflächen. Im Zuge dessen hoffen die anderen Abteilungen diese außergewöhnlichen Werkzeuge instrumentalisieren und synergetisch für andere Ziele und Projekte nutzen zu können.

Markus Antonietti, Peter Fratzl, Reinhard Lipowsky,
Helmuth Möhwald, Peter Seeberger

The Research Program of the Max Planck Institute of Colloids and Interfaces (MPI-CI)

Colloid and interface science focusses 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.

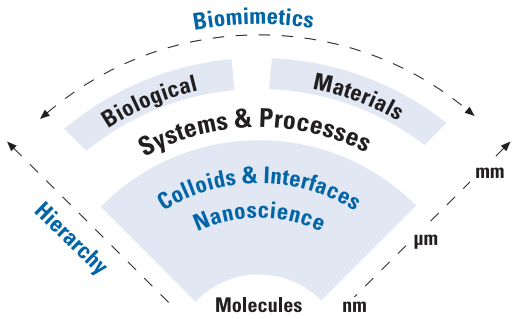


Fig. 1: Research in the MPI-CI focuses on structures and processes in the size range between nano and micro, the traditional domain of colloid and interface science, covering many levels from molecules to biomimetic materials and biological tissues.

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 MPI-CI 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.

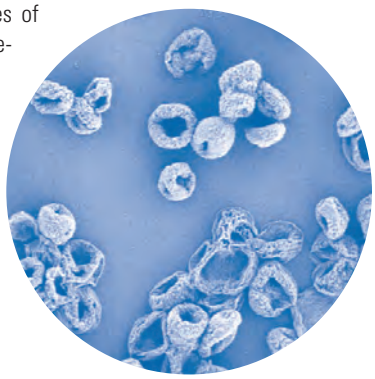
This interplay between experiment and theory is necessary in order to gain a deeper understanding of colloidal and interfacial systems. This understanding can then be used in order to improve the design of these systems, to optimize their performance, and to increase their reliability. In this sense, research at the MPI-CI 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 MPI-CI. 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 MPI-CI, based on the subsequent deposition of negatively and positively charged polyelectrolytes.

A large spectrum of experimental methods is used at the MPI-CI 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 MPI-CI. More details on the various methods are provided in the reports of the experimental groups.

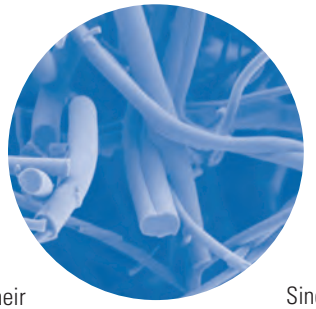
Biomimetic Systems

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 MPI-CI 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 formed from lipid or polymeric bilayers, and capsules existing of 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 MPI-CI has created the International Max-Planck Research School on Biomimetic Systems, complemented by a Marie-Curie Early Stage Training Network, described in detail on the next pages.

Since "interfacing" is a key issue in the set-up of controlled and functional colloidal superstructures, decoration of the surface of various building blocks with specifically interacting moieties is mandatory. While peptide codes and the decoration with complete biological recognition moieties is found widespread and in many variations, the Seeberger group has focussed on the synthesis of specific sugar and oligosaccharide moieties to establish recognition and interaction between biological systems but also for the interface between synthetic materials and biosystems. Peter Seeberger has designed diverse automated synthesis procedures towards such functional carbohydrates in the past, thus allowing to address problems as Malaria treatment or the synthesis of Heparin. We regard this approach of polysaccharide recognition and encoding as unique also for colloids and interfaces, and the other departments intend to instrumentalize these unique tools synergistically for other targets and projects.

Markus Antonietti, Peter Fratzl, Reinhard Lipowsky, Helmuth Möhwald, Peter Seeberger

The newest addition to the portfolio of the institute is the department "Biomolecular Systems" headed by Prof. Peter H. Seeberger. It has started its scientific work in January 2009. As this is not within the reporting period, there is no chapter on the outcome of this group. Nevertheless, as a part of the scientific profile there will be an introductory article discussing expectations and promises.

Wissenschaftliche Beziehungen

Kooperationen mit Universitäten:
Zwischen dem Max-Planck-Institut für Kolloid- und Grenzflächenforschung (MPI-KG) und der Universität Potsdam besteht seit Institutsgründung eine intensive und gute Zusammenarbeit. Prof. Antonietti, Prof. Fratzl, 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 und Prof. Seeberger an der Freien Universität Berlin. Darüber hinaus wurde Prof. Rabe vom Institut für Physik der Humboldt-Universität 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 Universtät Potsdam eingerichtet wurde und an der sich seit 2006 auch die Humbodt-Universität und die beiden Fraunhofer-Institute in Golm beteiligen. Der Sprecher der Schule ist Prof. Lipowsky, der die Schule 1999 beantragt hatte.

Zur weiteren Verstärkung der Zusammenarbeit wurden zwei Juniorprofessuren an der Universität Potsdam eingerichtet, besetzt durch Prof. Andreas Taubert (Kolloidchemie) und durch Prof. Matias Bargheer (Grenzflächen).

Das Institut ist über den Sonderforschungsbereich (SFB) 448 „Mesoskopische Verbundsysteme“ sowie dem SFB 760 „Muskuloskeletale 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 (BCRT) sowie der von der DFG-Exzellenzinitiative geförderten Graduiertenschule Berlin-Brandenburg School of Regenerative Therapies (BSRT). Eine Plattform für die Untersuchung biologischer Proben mit Synchrotronstrahlung wird in enger Kooperation mit der Universität Heidelberg aufgebaut und am Helmholtz-Zentrum Berlin für Materialien und Energie betrieben.

Großes Engagement gilt der Betreuung und dem Aufbau von Messplätzen an den Berliner Neutronen- und Synchrotronstrahlungsquellen sowie dem Deutschen Elektronen Synchrotron (DESY) in Hamburg.

Internationale und nationale Kooperationen:
Im Rahmen von europäischen Förderprogrammen, insbesondere dem 6. und 7. Rahmenprogramm der EU partizipieren Arbeitsgruppen des Instituts an Network of Excellence- (NoE), Marie Curie- und Specific Target Research Projects (STREP)- Maßnahmen. Insgesamt laufen zurzeit fünf EU-Projekte innerhalb des 6. und sechs EU-Projekte innerhalb des 7. Rahmenprogramms, davon zwei ERC Advanced Grants. Das Marie Curie Netzwerk über „Biomimetic Systems“ und das STREP-Netzwerk über „Active Biomimetic Systems“ wurden bis 2008 von der Theorieabteilung des MPI koordiniert. Weitere Informationen zu diesen beiden Netzwerken finden Sie unter www.biomimeticsystems.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.

Die Abteilung Grenzflächen unterhält zusammen mit der Chinesischen Akademie der Wissenschaften ein Internationales Labor in Peking und ein gemeinsames Labor mit dem National Institute for Materials Science (NIMS) in Tsukuba (Japan). Darüber hinaus betreibt sie seit 2008 ein „Laboratoire Européen Associé über „Sonochemie“ mit dem CEA-Institut für Separationschemie in Marcoule.

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 lief in 2004 das mit rund fünf Mio. Euro aus dem strategischen Innovationsfonds geförderte Projekt „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 und ist 2008 nach erfolgreicher Evaluation für eine zweite Förderperiode bestätigt worden.

Darüber hinaus kooperiert das Institut mit den Fraunhofer-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. Außerdem beteiligt es sich an dem vom BMBF geförderten Netzwerk GoFORSYS über Systembiologie sowie an dem von der DFG geförderten internationalen Graduiertenkolleg über „Self-assembled Soft Matter Nanostructures“.

Industriekooperationen, Verwertungsverträge, Ausgründungen

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

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-Netzwerken. Mit Einrichtung der Abteilung „Biomolekulare Systeme" hat das Institut sein Spektrum erweitert und den Fokus auf Biowissenschaften verstärkt.

Editorial Boards und Fachbeirat

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.

Editorial Boards:

- Applied Rheology (M. Antonietti)
- Advances in Colloid and Interface Science (R. Miller, Herausgeber)
- Advanced Engineering Materials (P. Fratzl)
- Biomacromolecules (H. Möhwald)
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- Polymer (M. Antonietti)
- Progress in Polymer Science (M. Antonietti)
- Review in Molecular Biotechnology (M. Antonietti)
- Soft Matter (H. Möhwald, Herausgeber)

Fachbeiräte:

- Adolphe Merkle Institute (AMI) Fribourg (H. Möhwald)
- Austrian Nano Initiative (H. Möhwald, Beirat und Jury)
- Berlin-Brandenburg School of Regenerative Therapies (BSRT) (P. Fratzl)
- DECHEMA Arbeitsgruppe über "Chemische Nanotechnologie" (H. Möhwald)
- Elitenetzwerk Bayern (R. Lipowsky)
- Fondation ICFRC, International Center for Frontier Research in Chemistry, Strasbourg (H. Möhwald)
- 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)
- Institute of Biophysics and Nanosystems Research of the Austrian Academy of Science (ÖAW), Graz (H. Möhwald, Vorsitzender)
- PETRA III microfocus beamline (P Fratzl)
- Photon Science Committee DESY (P. Fratzl, Chair)

Scientific Relations

Co-operations with Universities

The Max Planck Institute of Colloids and Interfaces (MPI-CI) and the University Potsdam maintain since its foundation intense and well-connected research co-operations. Prof. Antonietti, Prof. Fratzl, 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 and Prof. Seeberger at the Free University Berlin. 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 and the two Fraunhofer Institutes in Golm as well. The chairman 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 760 program "Musculoskeletal Regenaration" co-ordinated by Charité, Medical University, Berlin. The MPI is also member of the BMBF financed Berlin-Brandenburg Center for Regenerative Therapies (BCRT) and the Berlin-Brandenburg School of Regenerative Therapies (BSRT), funded by the Excellence Initiative of the DFG. Furthermore a platform for investigating biological specimens at Synchrotrons is set up together with the University Heidelberg and is run by the Helmholtz Centre Berlin for Materials and Energy.

Big engagement required also the maintenance and build-up of beamlines at the neutron- and synchrotron radiation sources in Berlin and the German Electron Synchrotron (DESY) in Hamburg

International and National Co-operations:

Several research groups take part in Networks of Excellence (NoE), Marie Curie and Specific Target Research Projects (STREP) within the framework of European programs, especially the 6th and 7th framework program of the EU. In total there are five EU projects within the 6th and six within the 7th framework program, including two ERC Advanced Grants. The Marie Curie network on "Biomimetic Systems" and the STREP network on "Active Biomimetic Systems" were coordinated by the Theory & Bio-Systems Department of the MPI until 2008. Further information is available under www.biomimeticsystems.de.

Beyond the collaborations described there exist bilateral and co-operation projects under assistance of the European Space Agency (ESA), the German Academic Exchange Service (DAAD), the German Research Foundation (DFG), German Israel Foundation (GIF) for Scientific Research and Development, the National Institutes of Health (NIH), VW- and Zeit-Stiftung with 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 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. 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). Furthermore there exists a Laboratoire Européen Associé about „Sonochemistry". It is run since 2008 together with the CEA Institute of Separation Chemistry in Marcoule.

Also the project "EnerChem", funded with 5 Mill. EUR by the strategic innovation funds of the Max Planck Society, has been successfully started in 2004. EnerChem is a research association, initiated by five Max Planck Institutes and coordinated by Prof. Antonietti of the MPI-CI. 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. After a successful evaluation in 2008 the reseach initiative has been approved for a second funding period.

Furthermore a co-operation 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. The institute also takes part in the systems biology network GoFORSYS, which is funded by the BMBF and the international graduate program "Self-assembled Soft Matter Nanostructures", which is funded by the DFG.

Co-operations with Industry, Application Contracts, Spin-Offs

Among many industry contacts co-operations with well-defined targets have been with BASF Coatings, Clariant GmbH, Degussa AG, Firmenich, Procter & Gamble, Servier and Schering AG. At present the MPI-CI upholds 46 patents. In the period from 1993-2006 six spin-offs have been launched: Capsulution Nanoscience AG, Colloid GmbH, Nanocraft GmbH, Optrel, Riegler & Kirstein and Sinterface.

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. With the establishment of the "Biomolecular Systems" department the scientific spectrum has been enlarged and the focus on biological sciences has been strongly intensified.

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.

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- DECHEMA Research Group on "Chemical Nanotechnology" (H. Möhwald)
- Elitenetzwerk Bayern (R. Lipowsky)
- Fondation ICFRC, International Center for Frontier Research in Chemistry, Strasbourg (H. Möhwald)
- Fraunhofer-Institute of 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 Biophysics and Nanosystems Research of the Austrian Academy of Science (ÖAW), Graz (H. Möhwald, Chair)
- Institute of Theoretical Physics, CAS (R. Lipowsky)
- Minerva Weizmann Committee (R. Lipowsky)
- PETRA III Microfocus Beamline (P. Fratzl)
- Photon Science Committee DESY (P. Fratzl, Chair)

Internationale Max Planck Research School (IMPRS) über Biommetische Systeme

Das Max-Planck-Institut für Kolloid- und Grenzflächenforschung (MPI-KG) koordiniert gemeinsam mit der Universität Potsdam seit 2000 die „Internationale Max Planck Research School (IMPRS) über Biomimetische Systeme". Die Schule wurde von 2004 bis 2008 um ein *European Early Stage Training (EST)* Netzwerk erweitert, das aus 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.

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 MPI-KG erforscht biomimetische Systeme im Bereich supramolekularer und kolloidaler Größenordnungen. Diese Systeme werden hauptsächlich durch die innere Architektur von Zellen inspiriert, enthalten viele, aus Ionen und kleinen Molekülen aufgebaute Nanostrukturen und weisen lineare Dimensionen zwischen einigen Nano- und vielen Mikrometern auf.

Die aktuelle Forschung über biomimetische Systeme am MPI-KG 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, Systembiologische Projekte.

Derzeit stoßen biomimetische Systeme als wissenschaftliches Topthema auf ein überaus großes, weltweites Interesse. 1999, als die Internationale Max Planck Research School (IMPRS) über „Biomimetische Systeme" 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" jetzt eine Popularität erlangt, die bis in die Werbung und den Film reicht. Aufgrund dieser rasanten Entwicklung zeigt Google bei Sucheingabe heute mehr als 800.000 Ergebnisse für „biomimetische Systeme" an. Dabei stehen unsere Initiativen bei diesem Suchbegriff mehrmals unter den zehn besten Treffern.

Lehrprogramme über Biomimetische Systeme

Das Max-Planck-Institut für Kolloid- und Grenzflächenforschung hat die große Bedeutung biomimetischer Systeme schon früh 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 der meisten Studenten reicht allerdings nicht für ein befriedigendes Grundwissen in der Biomimetik 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) über „Biomimetische Systeme" wurde 1999 von einem von uns (R.L.) eingereicht und von der Leitung der Max-Planck-Gesellschaft zunächst für einen Zeitraum von sechs Jahren bewilligt. Die Schule eröffnete daraufhin das erste Semester im Jahr 2000. Nach erfolgreicher Evaluierung im Jahr 2004 erhält die Schule eine weitere Förderung von sechs Jahren bis Ende 2012.

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 MPI-KG 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 Potsdam-Golm gezogen. Die Gruppen der Humboldt- Universität zu Berlin befinden sich in Berlin-Adlershof.

Lehrplan

Die Schule organisiert mehrere Lehrveranstaltungen pro Semester. Zum Einen gibt es allgemeine Kurse, um ein gemeinsames wissenschaftliches Basiswissen zu etablieren. Diese Kurse vermitteln die fundamentalen Prinzipien theoretischer, rechnerischer und experimenteller Arbeit auf dem Gebiet biomimetischer Systeme. Zum Anderen gibt es mehrere Kompaktkurse, die speziell auf bestimmte Themenbereiche ausgerichtet sind.

Bewerbung
Die IMPRS über Biomimetische Systeme akzeptiert im Allgemeinen Bewerbungen während des ganzen Jahres und das ohne besondere Fristen. Interessierte Studenten können über ein Online-Formular auf der schuleigenen Webseite ihre Anfrage übermitteln. Der Fragebogen bezieht sich auf relevante Punkte im Lebenslauf des Kandidaten. Ist dieser vollständig ausgefüllt, erhält der Koordinator der Schule (A.V.) die Bewerbung und leitet sie an die passenden Gruppenleiter weiter. Bei Interesse wird der Student aufgefordert, eine vollständige Bewerbung einzureichen.

Mitgliedschaft und Anrechnungspunkte
Doktoranden, die bei einer der Partnergruppen arbeiten, können sich für eine Mitgliedschaft bewerben, ganz unabhängig davon, welche Institution das Stipendium finanziert.

Mit der Mitgliedschaft bei der IMPRS akzeptiert man die Bedingungen bezüglich der Anrechnungspunkte. Jeder Kurs und jede Aktivität innerhalb der IMPRS berechtigt zu einer bestimmten Anzahl von Punkten. Hat ein Student die benötigten Punkte gesammelt und seinen Doktortitel erhalten, wird ein IMPRS-Zertifikat ausgestellt, das die Mitgliedschaft und Leistung bescheinigt.

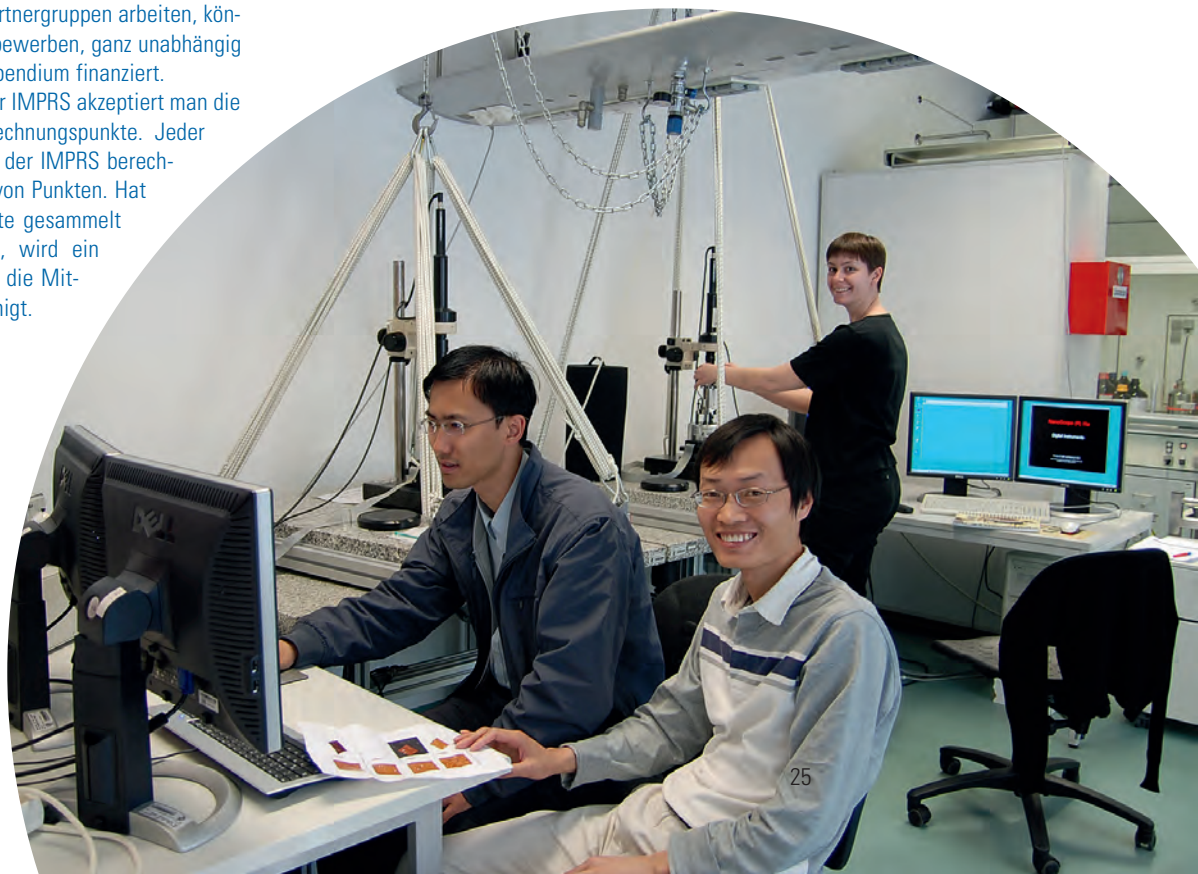
Doktorgrad
Studenten, die Mitglieder der IMPRS sind, sind immer als Doktoranden an einer der Partneruniversitäten eingeschrieben. Sie verteidigen ihre Arbeit vor einer Kommission, die aus Fakultätsmitgliedern der Universität und des MPI für Kolloid- und Grenzflächenforschung besteht und den Regeln der jeweiligen Universität unterliegt.

Internationalität
Die IMPRS über Biomimetische Systeme ist offen für Kandidaten aus aller Welt. Sowohl die IMPRS als auch das MPI für Kolloid- und Grenzflächenforschung sind sehr internationale Einrichtungen: Alle Vorlesungen und Aktivitäten werden in englischer Sprache abgehalten.

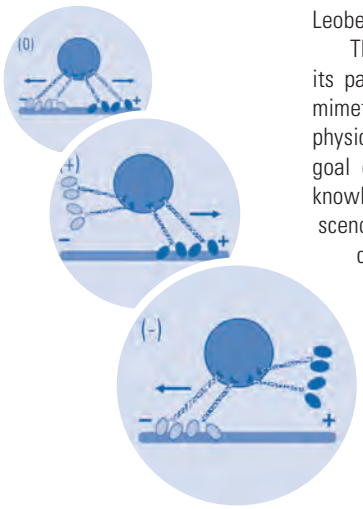
Internet
Weitere Informationen über den Lehrplan und die Zulassungsvoraussetzungen erhalten Sie unter:

www.bio-systems.org/imprs

Reinhard Lipowsky und Angelo Valleriani



International Max Planck Research School (IMPRS) on Biomimetic Systems



IMPRS on Biomimetic Systems

The MPI of Colloids and Interfaces has established, in the year 2000 together with the University of Potsdam, an International Max Planck Research School (IMPRS) on Biomimetic Systems. This activity was enhanced from 2004 to 2008 by a European Early Stage Training (EST) network which included six partner groups in Copenhagen, Düsseldorf, Edinburgh, Leoben, Milano, and Toulouse.

The IMPRS on Biomimetic Systems offers, together with its partner groups, 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 transcends the traditional boundaries between the different disciplines. The curriculum is based on courses, seminars and workshops with the participation of scientists who work at the cutting edge of this field.

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 IMPRS on Biomimetic Systems is focussed 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; bio-mineralization and bone; networks dynamics and evolution; systems biology projects.

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 internet search engines would not return any significant number of results. Now, 'biomimetic' has become a popular term that is mentioned even in movies and advertisements, and Google returns about 800000 results for 'biomimetic systems'! In fact, our initiatives on biomimetic systems appear several times among the top ten results.

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 recognized that the traditional training of most students would not provide a sufficient basis for doctoral studies in biomimetics. In addition there was a strong demand for multidisciplinary training from those students who want to work in this emerging research field.

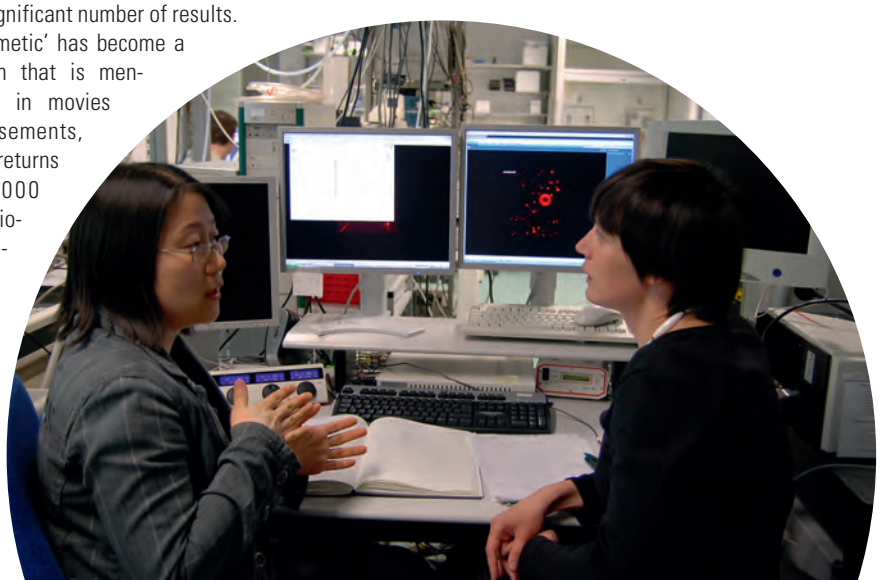
Thus, already in 1999, one of us (R.L.) submitted a proposal for the International Max Planck Research School on Biomimetic Systems (IMPRS) to the President of the Max Planck Society. This proposal was approved and the school started with its first semester in the year 2000. The school was originally approved for a period of six years until mid 2006. After a successful evaluation in 2004, our school will run for another six years until the end of 2012.

In our continuous effort to enlarge and strengthening our training activity we started in 2004 to coordinate a seven-partner Early Stage Training Network (EST) financed by the European Commission.

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", and one group from the "Fraunhofer-Institute of Applied Polymer Science".

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.



Curriculum
The school organizes several courses at each semester. There are general courses, intended to establish a common scientific background between all students. The general courses thus cover the fundamental principle of theoretical, computational and experimental work in the field of biomimetic systems.

In addition to these general courses, the school offers several compact courses that have a more specialized nature.

Recruitment
The IMPRS on Biomimetic Systems accepts applications during the whole year, in general without any deadline. Interested students send an inquiry by filling in an electronic form through the webpage of the school. The inquiry contains some basic information about the curriculum of the candidate. It reaches the coordinator of the school (A.V.) who contacts the possible group leaders. If there is an agreement that the candidate is potentially interesting he or she will be invited to send a full application.

Membership and Credit Points
PhD students working at one of the partner groups can apply for the membership of the school independently of the source that finances their fellowship.

Membership to the IMPRS means acceptance of the conditions concerning the Credit Points. Each course and each activity of the IMPRS gives right to a certain amount of credits. Once students have collected the necessary credits and have earned the doctoral degree, they receive an IMPRS certificate that attests their membership and their performance.

Doctoral Degree
Students that are members of the IMPRS are enrolled as PhD students at one of the partner universities. PhD students defend their research work in front of a commission that consists of faculty members from the university and the MPI of Colloids and Interfaces according to the usual university rules.

Internationality
The IMPRS on Biomimetic Systems is open to candidates from any country in the world. Both the IMPRS and the MPI of Colloids and Interfaces are highly international institutions: all lectures and activities are held in English.

Web Resources
Further information about the curriculum and the admission requirements, requirements can be found at:
www.bio-systems.org/imprs

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 Potsdam-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 zahlreiche Möglichkeiten, High-Tech-Technologien hautnah zu erleben und zu begreifen. Der Tag der Offenen Türen wird im Jahr 2009 am 19. 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

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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, brochures – 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 Sience Park Potsdam-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 2009 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 19. 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

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Wissenschaftspark Potsdam-Golm
Foto: Lutz Hannemann

*

→ Biological Materials
→ Biological and Biomimetic Materials
→ Bio-Inspired Materials

BIOMATERIALS

Research in the Department of Biomaterials

The Department of Biomaterials conducts interdisciplinary research at the interface between materials science and biology. The approach is to elucidate the basic mechanisms by which the hierarchical structure of a variety of biological or bio-inspired materials leads to mechanical performance. The principle goals are:

(1) to provide new concepts for developing new materials inspired from nature,
(2) to contribute to the understanding of the biological tissue itself, for example in the context of biomedical problems.

To tackle such questions, the members of the Department have very diverse scientific backgrounds, including mathematics, physics, chemistry, materials science, geosciences, biochemistry, wood science, botany, molecular biology and dentistry. The Department is organised into topical research groups, each of them concentrating either on a class of biomaterials (such as the plant cell wall or mineralized tissues) or on special methodology (such as synchrotron research or mathematical modelling). In this way, a expertise in a given field is maintained in each of the groups and strong scientific interaction and collaboration between them helps addressing scientific problems at the interface between various disciplines. Typically, these research groups comprise – in addition to the group leader – several doctoral students, postdocs, one or two technicians and responsibility for laboratories and heavy instrumentation maintained for the institute as a whole. In addition to the research groups, several independent postdoctoral researchers, some of them with individual grants from the Humboldt Foundation or other organisations, work on chosen scientific projects but without responsibility for a larger group.

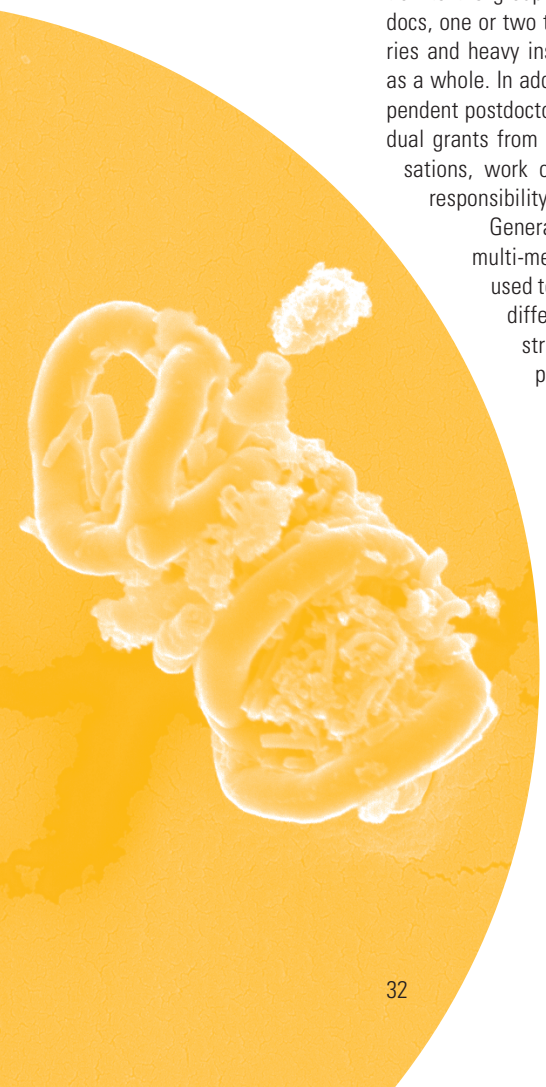
Generally, the experimental approach is based on multi-method imaging where different probes are used to image the same specimen. This combines different type of information, such as microstructure, chemical composition, mechanical properties in a position-resolved way with a resolution in the micron range. We are currently using scanning electron microscopy and scanning x-ray diffraction to characterize the micro- and nanostructure. We have established polarized and confocal Raman imaging to provide information on chemical composition and fibre orientation and we use nanoindentation 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 with hierarchical structure.

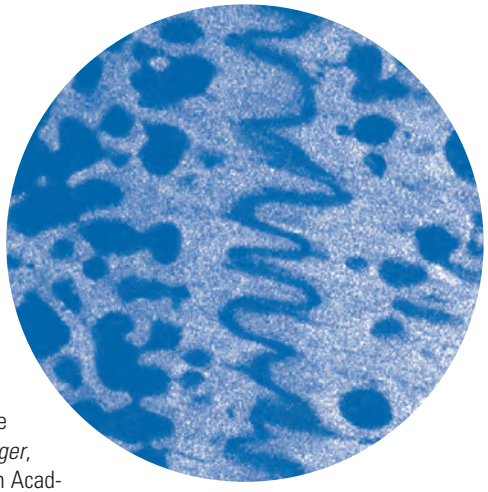
In a second type of approach, we study changes in a material (e.g. due to mechanical stress or to chemical or thermal processing) by time-resolved scattering or spectroscopy during mechanical deformation or thermal or hygroscopic treatment. This gives insight into the molecular and supramolecular mechanisms at the origin of the often outstanding properties of these materials. In some cases, this can be performed in the laboratory (e.g. with Raman or infrared spectroscopy or in the environmental scanning electron microscope), but in many cases synchrotron radiation is needed (e.g. for x-ray diffraction or small-angle scattering). A dedicated beamline end-station for scanning small- and wide-angle scattering and fluorescence spectroscopy has been set up over the last years at the synchrotron BESSY at the Helmholtz-Zentrum Berlin (see report by *O. Paris*).

The report from the Department of Biomaterials is structured in three sections, from biological to biomimetic research. Bone research is a major activity, addressing fundamental questions about the hierarchical structure of bone and its relation to mechanical performance as well as medical questions related to osteoporosis and to fracture healing. Bone is a tissue primarily composed of collagen, the most abundant protein in our body, and nanocrystals of carbonated hydroxyapatite, a calcium phosphate mineral. Fundamental questions about how bone deforms under external loads and how it hinders the propagation of cracks have been addressed during the last years in the research group led by *Himadri Gupta* on **hierarchical connective tissues** (p. 36). This work was extended to other collagenous tissues, such as the deer antler or tendon. A major achievement was the discovery of a shearing mechanism between mineralized collagen fibrils that protects fibrils from premature fracturing. *Himadri Gupta* moved at the end of 2008 to a lecturer position at Queen Mary University, London.

In addition, bone micro-structure is studied in the context of **bone material quality and osteoporosis** (p. 34) mostly in collaboration with the Ludwig Boltzmann Institute of Osteology (Vienna, Austria). The rationale behind these studies is that osteoporotic bone fractures, which have generally been associated with bone loss, may also be linked to (age- or disease-related) changes in the bone material itself. A wide portfolio of techniques has been established in the Department during the last years for the characterisation of bone biopsies from patients in clinical studies, for example. Currently, extensive work is done in establishing polarized Raman imaging for these purposes (see report by *Admir Mašić).*

An extensive collaboration in the field bone regeneration was established 2007 in the Berlin area by the SFB760 on musculoskeletal regeneration (financed by DFG) and the Berlin-Brandenburg School of Regenerative Medicine (a





graduate school funded in the framework of the German excellence initiative). These consortia are coordinated by the medical University Charité in Berlin and the Department of Biomaterials is actively involved with scientific projects as well as in the various steering boards. Scientific activities in the context of **bone regeneration** are reported by *Manjubala Inderchand* (p. 38) and include characterisation of structure and material properties of the fracture callus, as well as fundamental in-vitro studies of bone tissue growth on 3D scaffolds.

Theoretical modelling of bone formation, resorption, mineralisation and healing, as well as other research in the context of **mechanobiology** are reported by *Richard Weinkamer* (p. 40). A large fraction of this work is carried out in collaboration with the two consortia mentioned above (Ludwig-Boltzmann Institute, on the one hand, and the BSRT and SFB760 on the other). One of the highlights is the use of theoretical methods to extract information on the mineralisation kinetics from a bone mineral density distribution that can be measured with a single biopsy from a patient.

A second block of activities is summarized under the title of Biological and Biomimetic Materials. Structure and its relationship to mechanical function are investigated for a diversity of biological systems with the aim to extract principles as inspiration for the biomimetic design of new materials or systems. In the group led by *Ingo Burgert*, research on **plant biomechanics and biomimetics** (see p. 42) focuses on the plant wall, on its structure and properties and on developing ideas about how to generate new composites based on the design principles observed in plants. One of the interesting functions in this context is humidity-driven actuation. This plays an important role in plant actuation, in seed dispersal or in the generation of growth stresses.

Damien Faivre started in 2007 a research group working on magnetotactic bacteria containing magnetite nanoparticles for orientation in the earth's magnetic field. These particles are usually arranged in chains. Current research work on **molecular biomimetics and magnet biomineralization** (see p. 44) investigates possible differences between biogenic and artificial magnetite particles, as well as the role of proteins (in particular MamJ and MamK) for controlling the nucleation and growth of these particles and the formation of the chain structure.

Further research in biological and biomimetic materials is conducted in collaboration with external partners and by several independent postdoctoral researchers. The general topic is to understand the path **from micro-structure to mechanical function** (p. 46). *John Dunlop*, reports work on modelling tissue growth and plant movements, two topics with a close relationship to experiments conducted in the Department. *John Dunlop* has been Humboldt Fellow in the Department and is starting a new research group from the end of 2008. *Paul Zaslansky* describes his work, mostly based on x-ray and neutron tomography, to elucidate the relation between structural features in dentin, in enamel and at the dentin-enamel junction with the mechanical response of an entire tooth. Indeed, some of these structures may potentially be optimized for the tooth's function and should not be altered in restorations. *Notburga Gierlinger*, an APART fellow supported by the Austrian Academy of Sciences, is describing her work on the structure of the plant cell wall and on composites based on cellulose whiskers. In addition, theoretical work with external collaborators has brought new insights into the mechanical behaviour of layered and cellular materials which mimic biological materials such as glass sponges or cancellous bone. Some of this work is carried out with *Dieter Fischer*, Professor of Mechanics at the University of Leoben, who recently received a Humboldt Award to visit the Max Planck Institute of Colloids and Interfaces.

A last section summarizes the work of two research groups on bio-inspired materials. *Oskar Paris* reports on **mesoscale materials and synchrotron research** (p. 52). Interesting structures in cellulose- and chitin-based biological materials are revealed by micro-diffraction. The thermal transformation of such (mineral-loaded) biological materials generates ceramic phases. These transformations as well as condensation processes within silica mesopores are studied by in-situ diffraction techniques. Most of this research uses synchrotron radiation and, in particular, the possibilities of the µSpot beamline at the BESSY synchrotron (Helmholtz Centre Berlin) mentioned earlier. *Oskar Paris* has been directing the design and the construction of the end station at this beamline. With February 2009 he moved as full professor and chair of the Institute of Physics to the University of Leoben in Austria.

His responsibility for the operation of the µSpot beamline has been taken over by *Barbara Aichmayer* who is heading a group on **biogenic minerals and bio-inspired nanocomposites** since 2007. She reports (p. 50) on the self-assembly of proteins responsible for enamel formation and on the internal (nano)-structure of natural and artificial calcite crystals grown in the presence of polymers. The basic aims of her group are to elucidate how (occluded) polymers are controlling the growth and the properties of inorganic crystals.

Finally, it should be mentioned that almost all of the research in the Department of Biomaterials is based on collaborations, inside the Department, with other Departments in the Institute and with many outside partners around the world who all deserve our sincere gratitude for working with us in such a nice way.

Peter Fratzl
Director of the Department of Biomaterials

Bone Material Quality and Osteoporosis

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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
Since 2008: Corresponding member of the Austrian Academy of Sciences
Since 2009: Honorary Professor of Physics at Potsdam University

The fracture resistance of bone is a crucial issue in bone diseases such as osteoporosis and it depends on many levels of hierarchical structure of bone **(Fig. 1)**. Understanding the structural basis of bone material quality is, therefore, essential for the assessment of diseases such as osteoporosis, for a critical evaluation of current therapies and to aid in their more targeted development. Current research on bone quality in osteoporosis is carried out primarily in close collaboration with the Ludwig Boltzmann Institute of Osteology (Vienna, Austria).

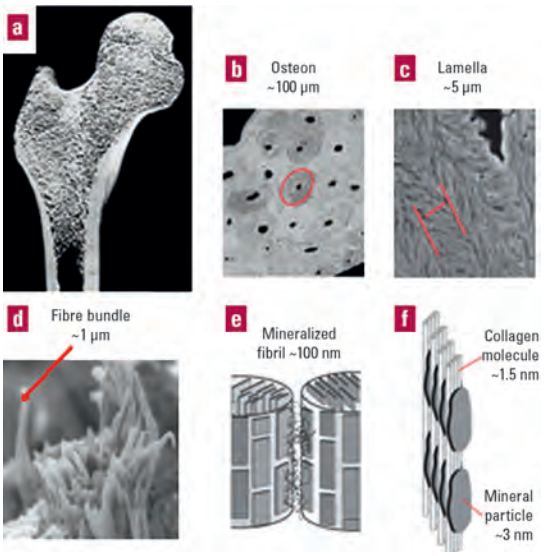

Fig. 1: Hierarchical structural levels in bone from the architecture of the human femoral head (a), osteonal structures surrounding blood vessels (b) via the lamellar (c) and fibrillar (d) organisations down to the nanoscale with mineralized fibrils (e) based on collagen and mineral nanoparticles (f). (from [1])

An ongoing activity is to assess the effect of osteoporosis treatments on bone material quality **[2]**. In recent years, the group has published a wide range of reference works, including an edited book **[3]**, several book chapters **[4-7]** and a review article **[8]**. In addition to the characterisation of the mineral distribution in bone tissue **(Fig. 2) [8]** and to the structural characteristics of the bone material at the nanoscale **[5, 6]**, particular attention has been paid to the validation of polarized Raman scattering for the characterization of collagen-based (mineralized) tissues **[7]**. The advantage of this technique is that it gives simultaneously information on the organic and on the inorganic component of bone. An analysis using a polarized laser beam gives additional information on local fibre orientations **[7]**. A more detailed description of these approaches is given on the next page by Admir Mašić, Postdoctoral Researcher supported by the Max Planck Research Award 2008 to PF.

Fig. 2: Bone trabecula from a biopsy visualized by back-scattered electron microscopy. Different grey scales indicate different mineral content. The local mineral content varies due to ongoing formation and resorption processes.

Bone can be present in a variety of forms fulfilling different mechanical functions. A first example is the deer antler, a particularly tough tissue (see Report of the group on mineralized tissues). A further example is the turtle shell which has been studied in collaboration with the group of Ron Shahar (Hebrew University, Israel). The shell of turtles is a shield which needs to be stiff at high loads but should provide sufficient flexibility for respiration and locomotion at smaller loads. We show that this seemingly contradictory requirement is met by a self-locking material, whereby stiff bony elements are connected by a much softer suture with a complex three-dimensional shape **(Fig. 3)**. A first description of this intricate tissue has just been published **[9]** (Highlighted as the Editor's Choice in Science 2009, 323: 438). Not only does this show a new level of organisation in bony tissue but this suture also shows an interesting principle of materials assembly with unusual mechanical behaviour.

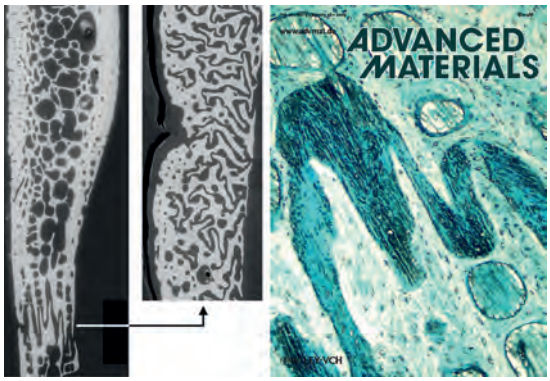

Fig. 3: Turtle shell consists of widened ribs (left) joined by an unmineralized suture (center) with a very complex shape. The central picture represents a cross-section through the suture region (arrow). The suture is filled with aligned organic fibres joining the bony parts (right). (from [9])

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Mapping Collagen-rich Tissue by Polarized Raman Spectroscopy

The collagen molecule is a fundamental structural building block for various types of natural tissues **[1]**. Its characteristic hierarchical structure, from atomic to tissue levels, allows for the fulfillment of a variety of mechanical functions, particularly in vertebrates. It is a major constituent of tendons and ligaments, as well as the organic matrix of bone and dentin – it is also present in skin and arteries. In all the aforementioned biological materials, the orientation of collagen fibers plays a fundamental role in the overall mechanical properties of the tissue. The significance of the collagen network and its architecture for normal physiological function can be witnessed when damage in one or both properties results in diseases such as osteoarthritis, skin cancer, osteogenesis imperfecta, etc. **[10]**

The aim of our work is to image collagen fibril orientation of tissues in situ by evaluating the molecular response within the tissue to a polarized laser source. For these purposes, we use Raman micro-spectroscopic and imaging analyses to elucidate collagen fibril orientation on micron scale.

Conventional single point Raman spectroscopy is inadequate to describe the chemical information and orientation distribution in relation to the macroscale. Recently, our group demonstrated the use of Raman imaging techniques in describing orientation and composition in cortical bone tissue **[7, 11]**.

In the present work we used polarized Raman micro-spectroscopy to obtain the diagonal, normalized components of the associated Raman tensor for the Amide I band in rat tail tendon (RTT). Obtained information was applied to process a series of Amide I Raman intensity images obtained with different orientation of incident laser polarization in Raman experiments. **Fig. 1** shows the map of the calculated orientation of the collagen fibers (direction of black lines). The length of the lines and the pixel color in the **Fig. 1** are related to the out of plane orientation of the collagen fibrils as well as the total amount of the Amide I band generating molecules. The calculated collagen orientation map is in good agreement with the fiber directions seen using optical microscopy **(Fig. 1A)**. The method can be applied to map collagen within other tissues, and in principal, it is possible to concurrently map other chemical components associated with collagen. The results demonstrate the versatility and potential of this analytical technique to image collagen fibril orientation within any tissue in-situ.

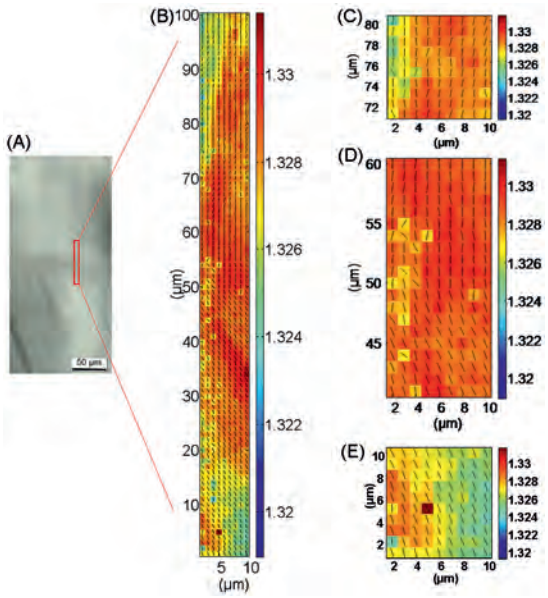

Fig. 1: In-situ polarized Raman mapping of the collagen fiber orientation in unstretched rat tail tendon (A) Optical microscopy image of the analyzed region where the crimp structure of collagen is visible (scale bar = 50 micron). (B) Map obtained by fitting 13 Raman images collected with different polarization angles of the incident laser light. The direction of arrows indicate the orientation of collagen fibers, their length represents the amplitude of the fitting curve, and the color code represents the average relative intensity of the Amide I band. (C), (D) and (E) Magnified regions of interest reveal specific structural changes in the tissue. Note the radical change in collagen fiber orientation corresponding to the crimp (at about 50 μm).

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Hierarchical Connective Tissues

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Biomineralized systems are hierarchically designed structures whose mechanical properties depend on multiple mechanisms at different length scales. They have a very high work of fracture, which is believed to arise from cooperative failure mechanisms at the nano- through micro level. We develop in-situ micromechanical and synchrotron-based methods to get answers as to how nature builds strong hierarchical systems. Our results find application in medical fields (for example to prevent bone fracture in osteoporosis) and in the design of new materials.

Nanoscale Fracture Mechanisms in Antler

Antler is a unique biomineralized organ in that it is annually regenerated completely and is used for a combat weapon during mating season by competing male deer. This makes it both an ideal model system for studying development of a biomineralized structure as well as an excellent example of a very high toughness structure tuned to function. Using in-situ synchrotron radiation combined with small-angle X-ray diffraction (SAXD), the (nanoscale) fibril strain was measured concurrently with macroscale tissue strain **[1]**. We observed a dramatic increase in SAXD peak width after mechanical yielding, indicative of decoupling between fibrils and heterogeneous fibrillar deformation. This result led us to a nanoscale model for the high toughness of antler, as shown in **Fig. 1**.

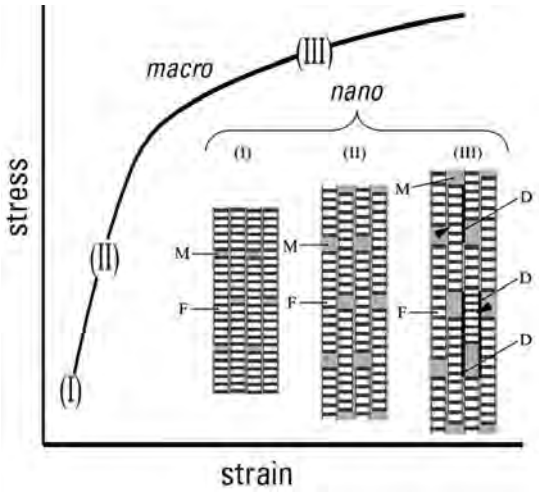

Fig. 1: Nanoscale model of heterogeneous fibrillar elongation in antler in the post yield(II – III) inelastic zone during macroscopic tensile deformation

High Microscale Mechanical Anisotropy of Bone

A crucial structural feature of bone (at multiple length scales) is the high structural anisotropy, with long mineralized collagen fibrils at the nanoscale assembling in twisted plywood lamellae at the micron level, which form cylindrical laminated structures (osteons) at the tissue level. In order to measure the mechanical anisotropy of the mineralized fibrils as far as possible, we considered individual structural components (bone packets) in the bovine bone periosteum. Using UV laser microdissection to cut out individual packets and thus avoid the complications of higher levels of hierarchy, microtensile tests were carried out on packets sectioned at different angles to the principle fiber axis. Our results reveal a very high mechanical anisotropy (100 to 1) in tensile strength and elastic modulus of these packets **(Fig. 2) [2]**.

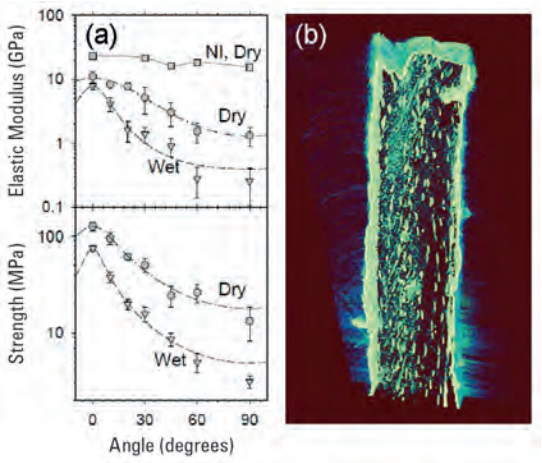

Fig. 2: High mechanical anisotropy of fibrolamellar bone packets as a function of angle to main fiber direction. A 3D X-ray microtomographic image of a bone packet is shown on the right.

Inelastic Deformation Banding in Bone

Little is known about the microscale processes operative during inelastic bone deformation, although these are expected to be quite different from those operating in simpler materials like alloys, polymers or ceramics. We developed a digital image correlation algorithm to measure the tissue strain distribution at the microscale (~100 µm) in bone **[3]**. Our result show that the elastic/inelastic transition is precisely the point, where, locally, one or more high deformation bands appear across the tissue, and eventual fracture occurs in these high-deformation regions **(Fig. 3)**. These results both provide important information on the microscale toughening mechanism as well as call into question use of simple parameters like ultimate fracture strain to describe fracture in bone.

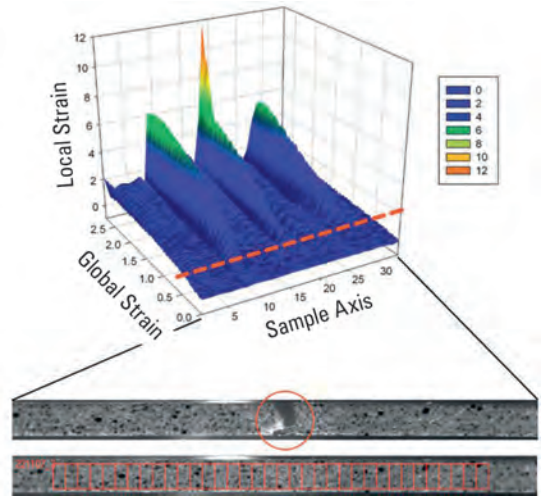

Fig. 3: High deformation banding occurring during inelastic deformation of bone. The lower two images show light-microscope images of bone-tissue and the tracking grid overlaid on the images to measure strain. The upper plot shows the local strain profile (vertical scale) along the sample axis as a function of global strain; 3 high-deformation bands are observed

Self Healing in the Connective Fibers of a Mussel

Some natural connective tissues exhibit remarkable mechanical and structural self-healing properties, and understanding the supramolecular origins of these qualities may help in designing synthetic self healing materials. The byssal threads of marine mussels are used as anchoring lines to secure the organism to the rock-bed in a wave swept seashore environment. While exhibiting elastic behavior at low strains (<15%), they can extend up to 100% strain without breaking, giving them properties comparable to Kevlar. They exhibit an acellular mechanical self-healing behavior over time after being stretched into the inelastic zone.

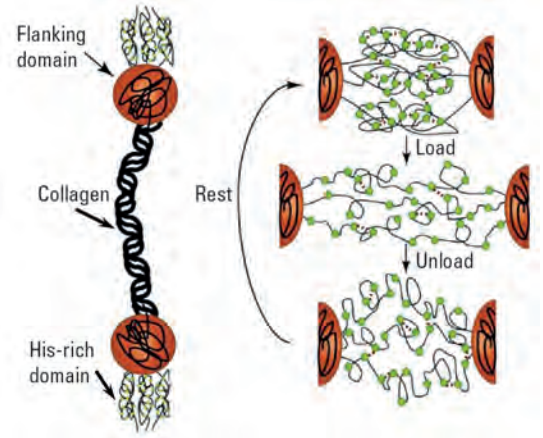

Fig. 4: Left: Molecular structure of the byssal fiber, indicating collagen domains, adjacent flanking domains and terminal histidine rich domains. Right: A molecular schematic of His-dependent healing in threads, by reformation of crosslinks.

We used synchrotron wide-angle X-ray diffraction with in-situ tensile testing to understand the molecular origins of this phenomenon. We find that the collagenous segment never exceeded strains of 2% despite the whole fiber exceeding over 70 % strain. This indicates a ductile non-collagenous component is crucial for the inelastic behavior. We propose that the histidine (His)-rich domains adjacent to the collagenous segment contain metal-His bonds, which are broken during inelastic loading and are eventually reformed during self healing **(Fig. 4)**. This suggest that by inserting molecular domains with such "sacrificial bonds" in series with stiff collagen segments, byssal fibers transform tendon-like fibers into much tougher and stretchable fibers with intrinsic self-healing capability **[4]**.

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Bone Regeneration

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Bone regeneration is influenced by biochemical, biomechanical as well as cellular mechanisms. Our general aim is to understand the fundamentals of underlying mechanism of new bone formation under different conditions such as in-vitro cell culture systems in scaffolds and in-vivo models of bone growth and development, and fracture healing conditions. Under in-vitro experiments, a biomimetic scaffolds with controlled architecture and varying pore size and shapes are used as substrate to investigate the kinetics of three dimensional growth of tissue produced by bone forming cells. Under in-vivo conditions, the new bone formation via fracture callus during bone healing process is studied, since little is known about the material properties of various types of tissues comprising the callus. Here we investigate the spatial and temporal sequential distribution of ultrastructure and mechanical properties of callus tissues. Both the projects have started in 2007 within the framework of Sonderforschungbereich (SFB) 760 focussed in Berlin with research partners from Charité-Universitätsmedizin Berlin and GKSS Institute for Polymer Research at Teltow. Although in medical terms the bone development from embryonal to mature bone is understood, the process of mineralisation and growth is not well known.

Bone Healing and Regeneration

After bone fracture, various cellular activities lead to the formation of different tissue types, which form the basis for the process of secondary bone healing. While the histological evaluations describe the spatial and temporal distribution of the various tissue types comprising the callus **(Fig. 1a)**, little is known of their material properties at various hierarchical level. We investigate the spatial distribution and temporal sequence of ultrastructure and mechanical properties of callus tissues over the course of bone healing by applying our established multi-method 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, nanoindentation and acoustic microscopy.

This project is in close conjunction with the researchers at Charité-Universitätsmedizin Berlin, (G. Duda, CMSC) where the bone healing experiments is carried out both in small and large animal models, as it is known that the tissue architecture is quite different in different animal species. In one of the fracture healing model in sheep bone, it has been shown that the indentation modulus (elastic modulus) maps in selected regions of callus are heterogeneous and follow the architecture of the trabeculae in the mineralized callus **(Fig. 1b)** and the average modulus value after 9 weeks of healing (end point) appears to be half of that of normal bone **[1]**.

This experimental result paved way to correct the wrong assumption used in theoretical modeling where in the modulus value of mineralized callus is assumed to be equal to bone. The spatial and temporal distribution of mineral content in the callus tissue, measured by quantitative back scattered electron imaging, also illustrates the ongoing bone formation and remodelling process. The structural investigations predicts the growth of mineral particles during healing process in callus tissue while there is a decrease in mineral crystal characteristics in cortex at the fracture gap, indicating dissolution of mineral from bone at fracture gaps **[2]**.

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. Other animal models will be investigated in this context.

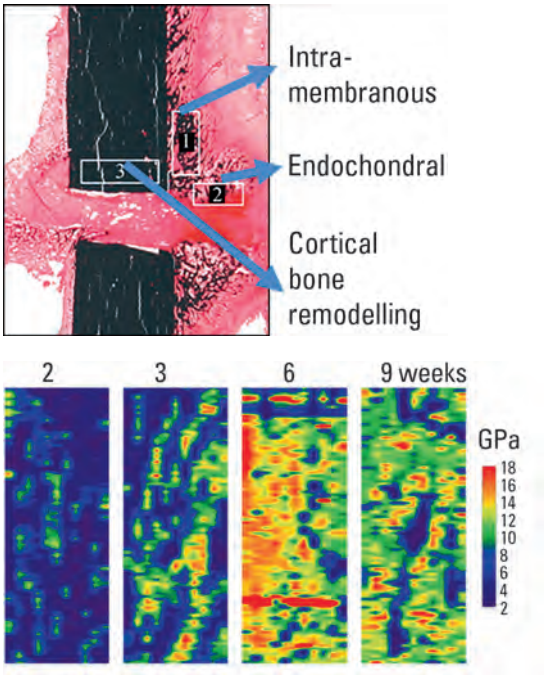

Fig. 1(a): The various tissues formed during fracture healing identified by histology (b) Indentation modulus maps of the intramembranous callus (region 1) over the course of healing in sheep fracture model.

Bone regeneration and remodelling around an implant is also studied in case of stainless steel and titanium nail implants using similar methodologies.

Bone Growth and Development

The knowledge how the mineral crystals in bone organise, nucleate and grow from the "birth of bone" (embryonal) is still poor. The study which aims to understand the development of the mineral properties, the mineral deposition and organisation from embryonal to mature bone has been now a part of graduate school in Berlin (cooperation with S. Mundlos, MPIMG). As it is already known that the genetic changes influence the material properties (mechanical properties) of bone **[3]**, the effect in embryonal bone level is not known and this will be studied further.

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.

Tissue Growth on Biomaterials of Controlled Geometry and Stiffness

Biomimetic scaffolds of controlled architecture are produced via solid freeform fabrication or rapid prototyping (RP) technique in which complex three dimensional (3D) structures can be produced directly from computer generated (CAD) design. The microstructure of the RP fabricated hydroxyapatite-chitosan/PLLA scaffolds were controlled by freeze drying process. The pre-osteoblastic cells cultured on scaffolds proliferated over the material and pores in multilayer and produced extra-cellular matrix in three weeks in both hydroxyapatite and polymer based composite scaffolds **(Fig. 2) [4, 5]**. The structure of the cell cultured scaffold allows designing the biomimetic scaffold with polymeric network inside the pores and enhances more cells to produce tissue compared to two-dimensional matrices **[6]**.

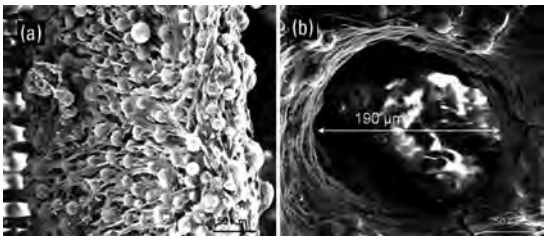

Fig. 2: SEM images of the cell cultured scaffold (a) showing the proliferated cells on one of the struts of scaffold and (b) cells filling up the pore channel with tissue and forming round canal.

The physical properties of scaffolds/substrates have a direct impact on cell proliferation and furthermore, on tissue formation. For this purpose a model system was established, which allowed in parallel microscopic observation as well as quantification of new tissue formation in a three-dimensional environment. The influence of various shapes and size of the pores in the hydroxyapatite scaffolds was studied and the tissue formation occurs in a way that is independent form the original shape, the tissue grows in round central canal form as observed with confocal laser scanning microscopy **(Fig. 3a) [7]**. 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 **(Fig. 3b)**.

Based on this information, various polymers with varying physical properties, especially, stiffness, are to be studied to analyse the effect on kinetics of tissue formation. Scaffolds from a series of polymer (polyurethane) with varying stiffness having various pore shapes and sizes was investigated to study the influence of the substrate stiffness on new bone tissue formation **[8]**. The kinetics study revealed that there are two stages of tissue growth compared to the stiffer hydroxyapatite material. The first early stage is dependent on substrate property and the second late stage is independent of the material **(Fig. 3c)**. Further studies will be based on other polymers with stiffness varying from kPa to MPa range that will be developed by our collaborating partners (A. Lendlein) from GKSS Institute for polymer research.

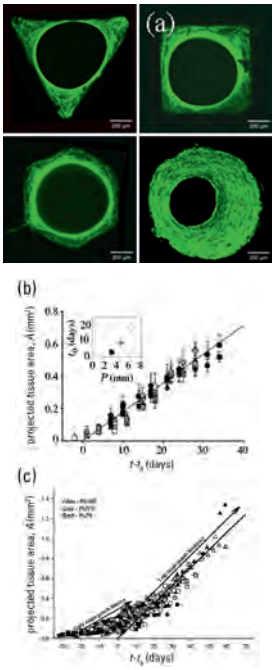

Fig. 3: (a) Extracellular matrix (ECM) tissue growth in 3D channels of various shapes in hydroxyapatite forming a round central channel, (b) showing that the growth is independent of shape and (c) tissue growth kinetics shows two stages in polymer scaffold.

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Mechanobiology

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Dynamical processes in bone are of great interest from both a materials and medical point of view. Computational models that take into account bone's structural hierarchy were employed to study the processes of mineralization, remodeling and fracture healing in bone. The second two processes are classic examples of mechanobiology **[1]**, in which cell action is mechanically controlled, the first being one which results in materials changes and thus mechanical changes within bone.

Bone Material Heterogeneity

On the microscopic length scale bone material quality is affected not only by the mean mineral content of the matrix, but also by the heterogeneity of the mineral content together with its spatial distribution. This heterogeneity of the mineralization results from the continuous remodeling, where a small bone volume is resorbed and replaced by an unmineralized bone packet. After the deposition, the mineralization process leads to an increase in the mineral content in the bone packet described by the mineralization law. The heterogeneous mineralization of trabecular bone is characterized by a frequency distribution, the bone mineralization density distribution (BMDD). We developed a mathematical model which relates the BMDD to the mineralization law **[2]**. Starting from the experimentally obtained BMDD of healthy human adults, the corresponding mineralization law was obtained. The investigation of a patient with a tumor-induced osteomalacia revealed profoundly disturbed mineralization kinetics **[3]**. The model was further applied to predict the full time evolution of the BMDD for two important clinical scenarios: menopause in women and anti-resorptive therapy. The simulations of increased bone turnover (menopause) resulted in a shift of the BMDD toward lower values of the mineral content with a significant transient broadening of the BMDD. Conversely, a decreased turnover (anti-resorptive therapy), caused the BMDD to shift towards higher values of the mineral content displaying a transient narrowing **[4]**. Additionally the model predicts the time evolution of the bone mineral density (BMD), which is used usually in the diagnosis of osteoporosis. The simulation showed that the strong reduction of the BMD after onset of menopause is only about half due to a loss in bone volume, whereas the other half is due to a reduction of the mineral content of bone **[4] (Fig. 1)**.

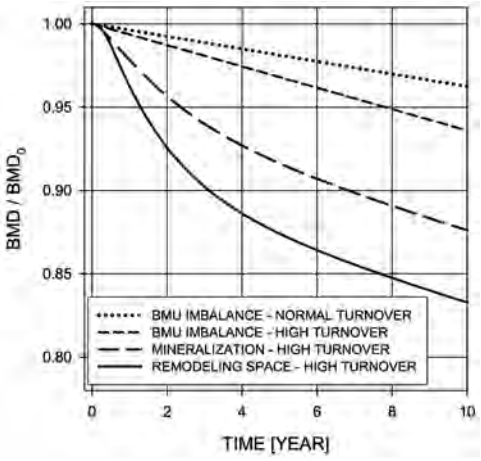

Fig. 1: Time evolution of the bone mineral density (BMD) after an increase in bone turnover simulating the onset of menopause (full line). An important contribution stems from the decrease in the mineral content, which is given in plot as the difference of the long and short dashed curves.

Adaptation of Trabecular Bone Architecture

On the mesoscopic length scale bone (re)modeling allows for the functional adaptation of the network-like architecture in trabecular bone to changes in the external loading. Consequently, the habitual loads on the bone should be reflected in its trabecular architecture. Together with anthropologists of the Max Planck Institute in Leipzig we used high resolution computed tomography and advanced image analysis techniques to analyze position resolved architecture in proximal femora of primates with different locomotor behaviors. The primates species analyzed were categorized as predominantly walkers, springers, brachiators or climbers. A local analysis was performed by moving a cubic volume of interest (VOI) of size $(5\,mm)^3$ throughout the proximal femur **[5]**. The obtained standard morphometric parameters like bone volume fraction (BV/TV), trabecular thickness (Tb.Th) and trabecular number (Tb.N) revealed two different mechanisms of trabecular bone adaptation **(Fig. 2)**. In highly loaded regions of the proximal femur, BV/TV increases by increasing the thickness of the trabeculae, while Tb.N remains constant. In less loaded regions, BV/TV decreases by reducing the number of the trabeculae while Tb.Th does not change. This reduction in Tb.N goes along with an increase in the degree of anisotropy, indicating an adaptive selection of trabeculae. The main orientation of the trabeculae in the femoral head is directed towards the femoral neck. Only the brachiator displays significantly lower trabecular anisotropy and a more radial arrangement within the femoral head.

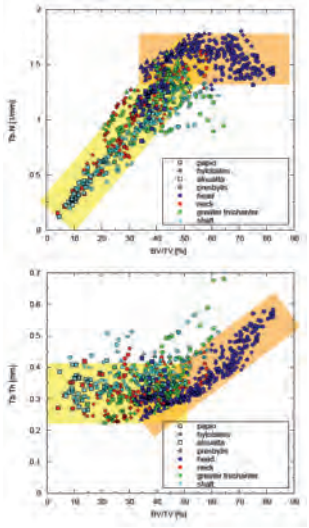

Fig. 2: Relation between the local bone volume fraction, BV/TV, and local trabecular number, Tb.N, and local trabecular thickness, Tb.Th, respectively. Data from all different primates and all different anatomical regions of the proximal femora are included (see figure legend). The primates differ in their locomotor behavior: papio (walker), hylobates (brachiator), alouatta (climber) and presbytis (springer).

Bone remodeling is thought to be mechanically controlled so that bone is removed locally where it is not mechanically needed and preferentially deposited at sites of high load (Wolff-Roux law). Using a computer model based on this mechanical control rule **[6]**, the best agreement between experimental data and simulation results were obtained, when a threshold for the local mechanical stimulus was assumed, above which strong bone deposition is activated **[7]**. In addition, we developed a stochastic model, which allows the extraction of information about the control of bone remodeling from measured trabecular thickness distributions (TTDs). In this Markov model each trabecula in a human vertebra is described by its thickness. Events of bone deposition or resorption change this thickness. Taking the TTD of young vertebrae as model input, a set of plausible remodeling rules for bone deposition/resorption could be obtained **(Fig. 3)**. These remodeling rules can then be used to predict the structural changes as described in the TTD as a function of age.

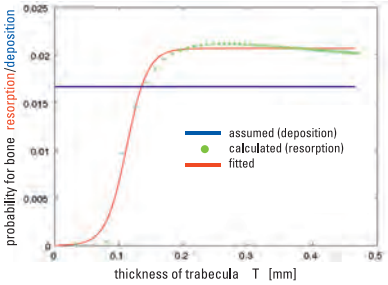

Fig. 3: Set of remodeling rules for the mechanical control of bone remodeling obtained on the basis of experimental data of the trabecular thickness distribution (TTD) of healthy bone. One remodeling rule has to be assumed the other can then be calculated.

Bone Fracture Healing

On the macroscopic length scale bone has the fascinating property to regenerate itself after a fracture, thereby returning basically to the prefracture state. Healing proceeds via a stabilisation of the bone fragments by the formation of an external callus and a succession of intricate patterns of different tissue types within this callus. Cell differentiation and the production of the different tissue types depend crucially on the local mechanical loading conditions **[8]**. We developed a computer model based on mechanobiological cell differentiation rules to be able to predict the course of healing in different scenarios. Beforehand we performed an analysis of healing data obtained from sheep to obtain quantitative data for comparison with simulations. An animal study of fracture healing within sheep was performed by our collaboration partners at the Charité, Berlin. The healing process in the tibia was monitored by means of longitudinal histological sections at 2, 3, 6 and 9 weeks postoperatively. The assembling of these histological sections to a succession of images that show the course of normal bone healing is significantly hampered by individual differences between the sheep. **Fig. 4** shows from the final result three from six obtained images displaying different stages in the healing process: the formation of new bone at the outer periosteal side, the development of cartilage within the fracture gap, the formation of a bony bridge at the outer side of the callus leading finally to a complete ossification.

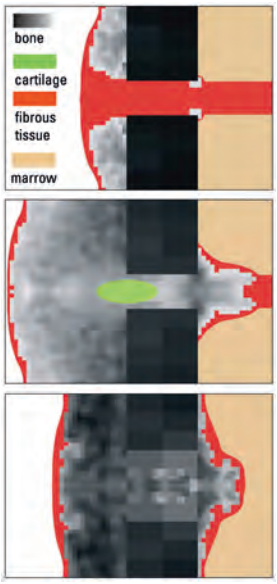

Fig. 4: Three different stages in the healing process of a long bone in sheep. The longitudinal sections through the cylindrical bone filled with marrow (only the left side is displayed) show the two bone fragments (black). Healing occurs by formation of a callus and an intricate temporal and spatial pattern of different tissue types.

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Plant Biomechanics and Biomimetics

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2000: PhD, Wood Science (University of Hamburg) Thesis: The mechanical relevance of rays in the living tree
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The research group Plant Biomechanics and Biomimetics investigates structure-function-relationships of plants at the micro- and nanoscale. 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 and is also a valuable source for extracting biomimetic principles.

Cell wall properties and plant actuation systems are analyzed to better understand the underlying principles and to utilize the gained knowledge for the design of innovative biomimetic materials.

Cell Wall Structure and Function

Plant cell walls consist of just a few nanometer thick cellulose fibrils as well as a matrix of hemicelluloses, pectins, lignin, and structural proteins. Their mechanical performance 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.

Our objective is to characterize this nanocomposite, in order to gain better insights into optimization strategies of living plants as well as into the material design as such. For this purpose we investigate primary cell walls of Arabidopsis hypocotyls and secondary cell walls mainly from spruce and aspen both in natural condition as well as genetically, chemically and enzymatically modified. The methods utilized are microtensile tests combined with X-ray scattering, Raman spectroscopy, FT-IR microscopy and Environmental Scanning Electron microscopy. Collaborations have been established in the framework of the EU-Project CASPIC as well as with the MPI for Molecular Plant Physiology MPI-MP), Potsdam.

In terms of primary cell walls of Arabidopsis we have continued and intensified our collaborations with plant physiologists, biochemists and biotechnologists to draw synergisms from the unique combination of enzymeology and genetic engineering on one hand and micromechanical characterization on the other hand.

In collaboration with the Markus Pauly Lab (now Michigan State University) we work on hemicelluloses in primary cell walls, mainly xyloglucan which is believed to build a load-bearing network together with the cellulose fibrils. Micromechanical analysis was contributed to a study on *Arabidopsis thaliana* deficient in xyloglucan in the primary cell walls due to the disruption of two *xylosyltransferase* genes. The obtained results challenge the common cell wall models **[1]**.

A further focus in primary cell wall research is on cellulose fibril orientation and its control by the plant. In collaboration with Staffan Persson from the MPI-MP we work on Arabidopsis plants which possess alterations in the cytoskeleton or in the cellulose synthase complexes due to I) chemical treatments and II) genetic modifications. In the framework of EU project CASPIC we work on transgene Arabidopsis plants with alterations in the protein structure of the cellulose synthase complexes (cesA2, cesA5, cesA6, cesA2/5 and cesA2/6) provided by the Lab of Herman Höfte (INRA-Versailles).

In terms of secondary cell walls further in-situ techniques have been established which combine micromechanical straining with nano- and microstructural observation. One achievement was a microtensile tester coupled with a cooling stage which allows mechanical tests of biomaterials in a fully hydrated state in a chamber of an Environmental Scanning Electron Microscope (ESEM), **(Fig. 1)**.

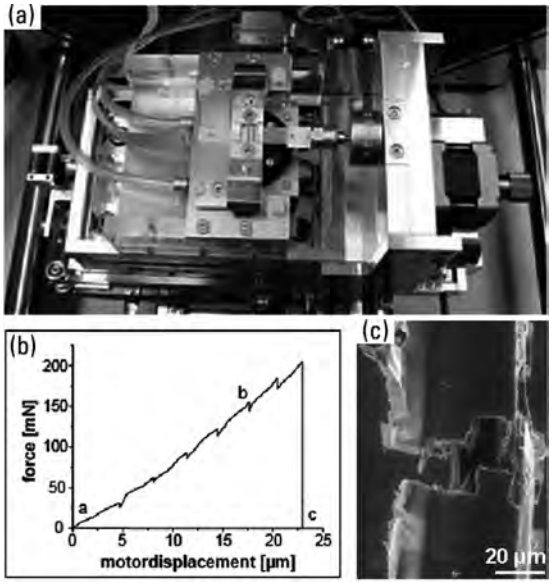

Fig. 1 (a) Tensile tester to be operated in the ESEM chamber; (b) Force-displacement curve of a single wood fibre (small load drops appeared when images were taken); (c) Single wood fibre after fracture [2].

In the framework of the EU project CASPIC transgene aspen plants with alterations in cellulose and lignin composition which had been provided by the Plant Science Center in Umea, Sweden (Lab Björn Sundberg) are investigated with respect to cell wall nanostructure and mechanical performance. Further genetically modified plants will be studied I) to learn about the control of cellulose fibril orientation in secondary cell walls and II) to better understand the cellulose fibril/matrix interactions in the cell wall assembly.

Exemplary studies on secondary cell wall led to a better understanding of structural and mechanical adaptations across growth rings in living trees **[3]** as well as to new insights into the cell wall nanostructure of softwood by means of cellulose fibril organisation **[4]**.

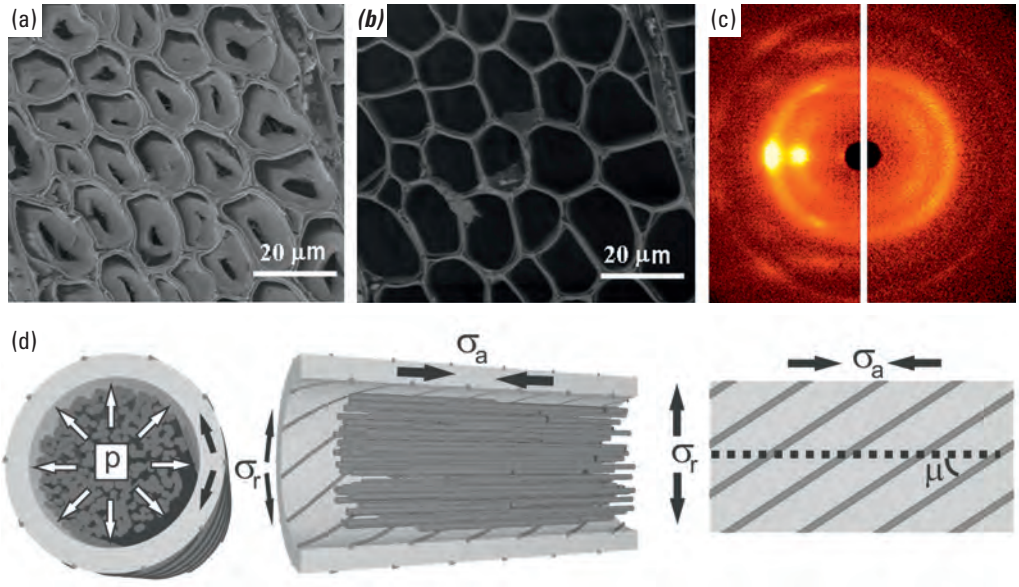

Fig. 2: (a) Effect of enzymatic treatment on the tension wood fibres. Scanning electron microscopy image of a a) cross-section of the native tension wood tissue with cell lumina almost completely filled with G-layers; (b) SEM image of the same tissue after enzymatic treatment with complete degradation of the G-layers; (c) WAXS diffraction pattern of poplar tension wood with G-layers (left) and after enzymatic removal of the G-layers (right). (d) Schematic drawing of the stress generation mechanism. The pressure p generated by the swelling of the G-layer is transferred into a circumferential hoop stress σ_r, within the cell wall which is converted into an axial tensile stress σ_a [7].

Stress Generation and Plant Movement

Investigations on directed movements of plants at long time scales (wheat awns, reaction wood of trees) which do not require any metabolism but are triggered simply by the swelling or shrinking of the cell walls have been conducted in close cooperation with Peter Fratzl **[5]**, **[6]**.

In a recent study we examined the underlying principle of stress generation in tension wood of poplar **(Fig. 2)**.

Tension wood enables hardwoods to generate very high tensile stresses on the upper side of a bending organ such as to pull leaning stems and branches upwards. The tension wood fibres tend to contract longitudinally during differentiation which generates high longitudinal tensile stresses. A gelatinous layer (G-layer) filling the lumen of the fibre is believed to be the operative part of the tension wood fibre. The fundamental question is how the length of tension wood fibres can be reduced by a G-layer consisting of axially oriented almost non contractile cellulose fibrils. This can be explained by an interaction with the spiral arrangement of cellulose fibrils in the secondary cell wall, by which the circumferential hoop stress is converted into a contraction of the cell along its length. It has been shown in a mechanical model that the optimal spiral angle for the generation of longitudinal contractile stresses is close to the observed microfibril angle of ~36°. Hence, the combination of an axially stiff and laterally swellable G-layer with a suitable cellulose microfibril angle in the secondary cell wall is responsible for the generation of considerable high tensile stresses in poplar.

Bio-inspired Materials

In the field of biomimetic research we finalized the work carried out in cooperation with the University of Freiburg (Lab Thomas Speck) on gradient transitions in arborescent palms with *Washingtonia robusta* as a model organism. It has been shown that a stiffness gradient is accommodated by the specific cell and cell wall structure of the stiff vascular fibres bundles which helps to avoid critical stress discontinuities and separation of the material at the interface to the soft parenchymatous tissues **[8]**.

Two projects on synthetic systems which are inspired by the fibre composite structure of plant cell walls are ongoing. Together with colleagues from the Department of Interfaces (Labs Dayang Wang, Rumen Krastev) we produce and characterize hydrogels which should become anisotropic and switchable due to the embedding of fibrillar components (DFG project).

In cooperation with colleagues from the Department of Colloids (Lab Helmut Schlaad), partners from the University of Bayreuth (Lab Andreas Fery), the University of Freiburg (Lab Thomas Speck), and from the ITV Denkendorf (Lab Markus Milwich) we develop innovative glass fibre composites in the framework of a BMBF project. Here the design of the interface between glass fibre and resin matrix is inspired by the embedding of cellulose microfibrils in the plant cell wall.

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Molecular Biomimetics and Magnet Biomineralization

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The formation of inorganic materials with complex form is a widespread biological phenomenon (biomineralization) that occurs in almost all taxonomic groups from prokaryotes to humans. Spectacular examples of biomineralization are found in magnetotactic bacteria that not only synthesized magnetite or greigite nanoparticles with a great variety of morphology within dedicated organelles called magnetosomes **(Fig. 1)**, but also arrange them in one or more chains in order to create an ensemble with enhanced magnetic properties **(Fig. 2) [1]**. These complex structures made of assembled biomineralized magnetic nanoparticles reveal our limited understanding of a fundamental question: How does a cell translate DNA sequence information into patterned three-dimensional organization?

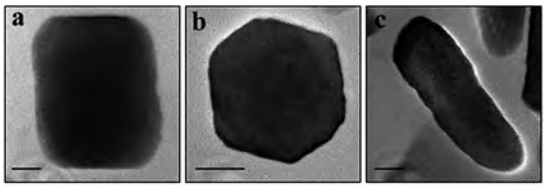

Fig. 1: Possible morphologies observed for magnetosomes based on high-resolution TEM images: A parallelepipedal projection of a possibly peudo-hexagonal prismatic morphology,B hexagonal projection of a possibly cuboctahedral crystal and C tooth-shaped (anisotropic) magnetosomes (the scale bar represents 20 nm).

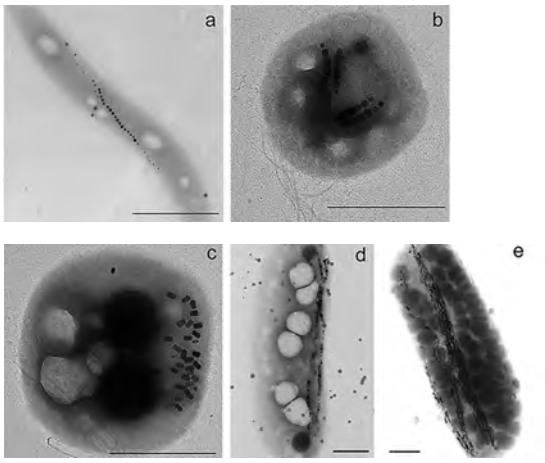

Fig. 2: TEM images showing the diversity of morphologies of magnetotactic bacteria and of the arrangement of magnetosomes (scale bar 1 µm). Morphologies include spirilla (a), cocci (b and c), rod-shaped (d) and vibrio-shaped microorganisms. Magnetosomes can be arranged in one (a) or several chains (b, d and e), or formed clusters (c).

Magnetotactic bacteria have thus mastered the combination of two contradictory capabilities: the biosynthesis of complex structures with high fidelity, and the seemingly infinite variation of this process. Consequently, magnetosomes are typically the result of highly efficient but complex natural processes that provide an ideal basis for developing biomimetic concepts towards new classes of magnetic components based on nanoparticles and their assembly.

Biological Materials

We, first, developed a technique that enables the study of magnetosome formation and assembly independently of cell growth **[2, 3]**. In the last months, the crystal structure of magnetosomes was studied by wide angle X-ray scattering with Synchrotron radiation in order to obtain information about a possible difference between biogenic and abiotic (synthetic) magnetite. Our first results indicate a reduced but clear isotropic lattice distortion of the magnetosomes relative to the inorganic magnetite control **(Fig. 3)**. Moreover, opposed peakshifts were observed in biogenic vs. abiogenic magnetite through annealing at 400 °C under inert atmosphere **(Fig. 3)**.

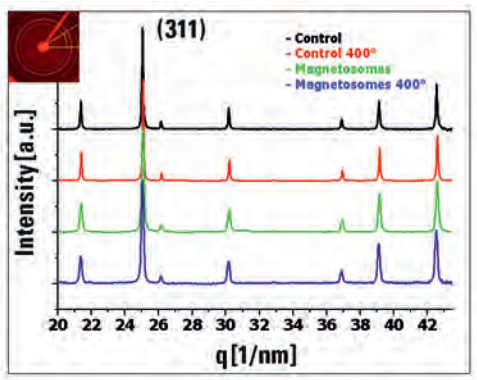

Fig. 3: Azimuthal integrated patterns of samples analyzed at the µ-SPOT Beamline of the BESSY synchrotron facility. In inset, the diffraction patterns of the abiotic magnetite control are presented.

Indeed, while the synthetic magnetite shows a reduction of the lattice parameter after the treatment, the treated magnetosomes exhibit an increased lattice parameter when compared to the original magnetosomes. Thus, besides side and surface effects that cannot be neglected so far, it seems that the magnetosome membrane not only serves as biological factory for the proteins responsible of magnetite formation, but also might play an unexpected mechanical role over the encapsulated biogenic magnetite nanocrystals.

Biomimetic Materials

Several putative magnetite biomineralizing proteins are found within the magnetosome membrane and/or attached to the crystals. Their respective roles are unclear as most show no or little homologies with other proteins from non-magnetic organisms. The protein MamJ is known to mediate the assembly of magnetosomes in vivo **[4]**. However, MamJ is an acidic protein that might interact with iron ions in vitro thereby affecting the synthesis of magnetite. Thus, recombinant MamJ proteins are currently investigated in vitro regarding their potential effects on magnetite crystal growth, size and morphology. Moreover, we are interested in the arrangement of the magnetic particles. MamK is a filamentous Actin-like magnetosomal protein sharing significant homology with bacterial cytoskeletal proteins such as MreB and ParM. Understanding the functionality of MamK is predicted to be critically important to the integrity of the crystal chains during in vitro biomimetic assembly. Cloning, overexpression and isolation of MamK are currently underway to aid physical patterning of the biomimetic nanoparticles.

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From Microstructure to Mechanical Function

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This section reports results from external collaborations on biological and biomimetic materials, as well the work of several independent postdoctoral researchers: John Dunlop, Humboldt Fellow working on the development of internal stresses in biological tissues, Paul Zaslansky studying the three-dimensional microstructure of teeth and Notburga Gierlinger, an APART fellow studying plant cell walls as inspiration for nanocomposites.

Biomimetic materials research is a rapidly growing field **[1]** where design principles of natural materials are studied, modelled and used to imagine new types of artificial materials. A wide range of topics is covered, for example, in a special issue of Advanced Materials co-edited with Joanna Aizenberg from Harvard University **[2]**.

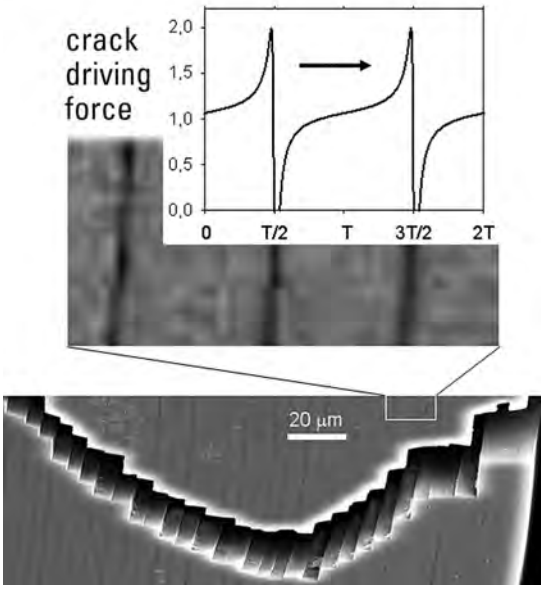

Fig. 1: The driving force for a crack propagating in a multilayered material with periodically varying elastic modulus is vanishing close to the minimum of the modulus. The example above shows a layered bioglass spicule with a series thin protein interlayers (dark grey). The calculation is done for a modulus ratio of 6 between the stiff and the soft layers [4]. The arrow shows the propagation direction of the crack.

In the years 2007/08, the hierarchical structure and the mechanical properties of silica sponges were continued to be studied in an ongoing collaborative project with Joanna Aizenberg and with colleagues at UC Santa Barbara **[3, 4]**. Additional details of the sponge skeleton architecture were discovered **[3]** and the fracture behaviour was analysed using an indentation method **[4]**. Cracks were seen to be stopped at the protein interfaces separating concentric silica layers in the spicule (see also bottom of **Fig. 1**). In this way, the inherent brittleness of glass is dramatically reduced, an effect which might be quite interesting from a practical point of view. This toughening principle was analysed theoretically together with the group of Dieter Fischer from the University of Leoben (Austria), currently Humboldt Senior Fellow in the Department. Using fracture mechanics concepts, it was shown that the crack driving force in a material with periodically varying elastic modulus may vanish close to the minimum of the modulus **[5]**. This means that a crack would effectively stop in the soft layer before a new crack is nucleated in the next layer, which also explains the stepwise propagation of the crack in silica spicules **(Fig. 1)**.

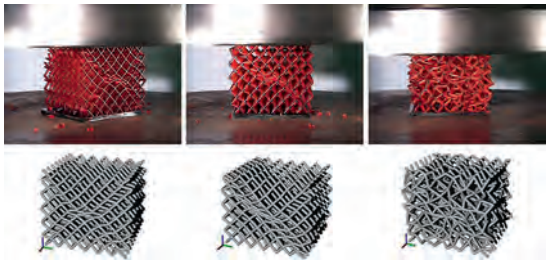

Fig. 2: Strut architectures built by rapid prototyping (top) or in the computer (bottom). Mechanical compression leads to strain localisation that depends on the degree of disorder in the strut arrangement [6]

Numerical modelling was also used in another project carried out in collaboration with the Vienna Technical University. Materials based on strut architectures with different degrees of randomness were built with rapid prototyping and their mechanical behaviour tested experimentally **(Fig. 2 top)**. In addition, deformation behaviour was simulated by a numerical model **(Fig. 2 bottom)**. It was shown that the major reason for strut failure is strain localization in shear bands (very well visible in **Fig. 2**) and that the localization is reduced with increasing randomness in the structure **[6]**. Such considerations are of great importance for the understanding of osteoporotic fractures in human vertebra, for example.

Finally, the structural basis and the mechanism of the movement of wheat awns **[7]** have been further studied in collaboration with Rivka Elbaum, a former Humboldt Fellow in the Department and now at Hebrew University in Israel. These awns perform a sort of swimming movement with cyclically changing air humidity by motor cells which expand or contract passively as a result of air humidity. It was shown that these motor cells have a multilayered cell wall structure **(Fig. 3)** with alternating cellulose fibril orientations in each layer **[8]**. The microscopic mechanism of the actuation turns out to be strongly related to these fibril angles with respect to the cell axis **[9]**. Depending on the fibril angle distribution in the cell wall, individual cells are expected to either shrink or expand in longitudinal direction. The (compressive or tensile) force also depends largely on this angle **[9]**

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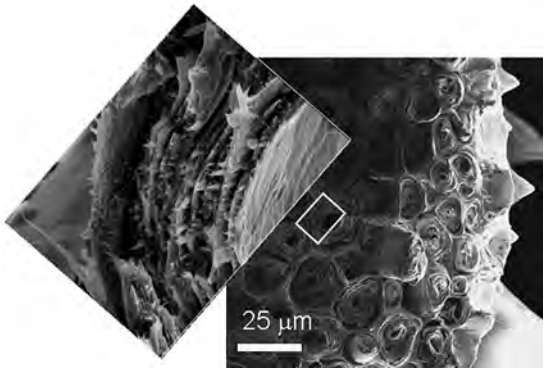

Fig. 3: Scanning electron microscopic picture of the actuating part of a wheat awn. The enlargement (left) shows the multilayered structure of the cell wall.

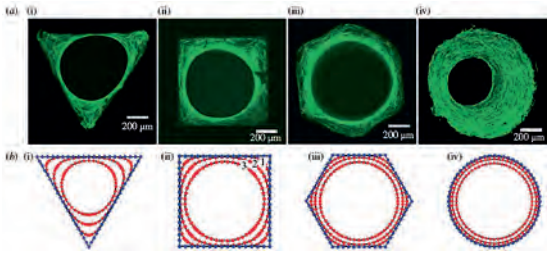

Fig. 4: (a) Tissue formed in three-dimensional channels (with actin fibres stained) after 21 days (i–iii) and (iv) 30 days of cell culture. (b) Numerical simulation of tissue formation within channels of various shapes. The lines (early time point 1, ongoing times 2 and 3) mark the simulated development of tissue formation (from [10]).

Modeling Stresses in Tissue and Tissue Growth

The work on the geometric control of tissue growth and stress development in plant organs discussed in the following is to be continued and expanded in the new research group Biomimetic Actuation and Tissue Growth, started at the end of 2008.

Recent studies have shown that in addition to biochemical signals, cells can respond also to physical signals such as the stiffness and shape of their environment. Research done in the Bone Regeneration Group of Manjubala Inderchand has shown that the rate of cell proliferation and new tissue growth in osteoblast cultures depends on the geometry of the environment in which the cells are growing. Osteoblast cell cultures were run in scaffolds of different channel shapes and showed that regions of higher negative curvature promoted more tissue growth than those of smaller curvature. This suggested that the growth process is controlled by local curvature, a well known phenomenon in materials physics. Simple simulations of curvature controlled tissue growth were run and closely matched the tissue growth patterns seen in experiment **[10]**. In particular, even though the local growth rate was geometry dependent, the global growth rate was found to be independent of shape, in both experiment and numerical simulations. These results may seem to be somewhat contradictory to the idea of curvature driven growth, however as the average mean-curvature of the prismatic channels tested are all the same then the average growth rate is independent. This is of particular importance in the design of scaffold materials for bone regeneration in addition to improving the understanding of the process of bone remodelling and fracture healing. This work is currently being extended (in collaboration with Prof. Dieter Fischer) to account for the coupling of stresses which develop in the tissue during growth.

Materials that can actuate complex motion or develop high stresses are particularly interesting with respect to potential application in MEMS, valves, artificial muscles and microfluidic systems. Of technical interest are the passive actuation systems found in plants which are mainly based on dead tissue. One example that can generate high stresses due to shape changes are the tension wood fibres found in the upper parts of branches of hardwoods studied in the Plant Biomechanics Group of Ingo Burgert. In many species the lumens of the tension wood cells are almost completely filled with an extra layer of parallel oriented cellulose (the G-layer), with the outside cell wall consisting of spirally wound cellulose. We were interested in understanding the stress-strain curve of tension wood before and after enzymatic treatment to remove the G-layer **[11]**. Un-treated wood, displayed zigzag oscillations in stress, much akin to the Portevin Le Chatelier effect, which disappeared after removal of the G-layer. By considering the G-layer as a load bearing element only weakly bound by frictional constraints to the cell wall, we could model the oscillatory stress-strain response of the tissue. The weak binding of the G-layer to the cell wall supported the idea that the G-layer is responsible for tensile stress generation. Upon hydration the parallel G-layer fibres swell pushing against the outer cell wall. The circumferential stress is converted into a contraction of the cell along its length resulting in generation of a high tensile stress **[11]**.

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Studies of Human Teeth: 3D Structure-Function Relations

Much is still unknown about the interplay between structural variation within human teeth (dentine, enamel) and the long-term durability – with no remodelling/healing – in the oral cavity. This durability may depend to a large extent on the subtle variations in microstructure and elastic and fracture properties of dentine **[12]**. Recent advances in coherent X-ray imaging and tomography are allowing us to match microstructure findings obtained by 2D methods (light and electron microscopy, speckle interferometry) with 3D-bulk scattering analysis (small angle x-ray scattering).

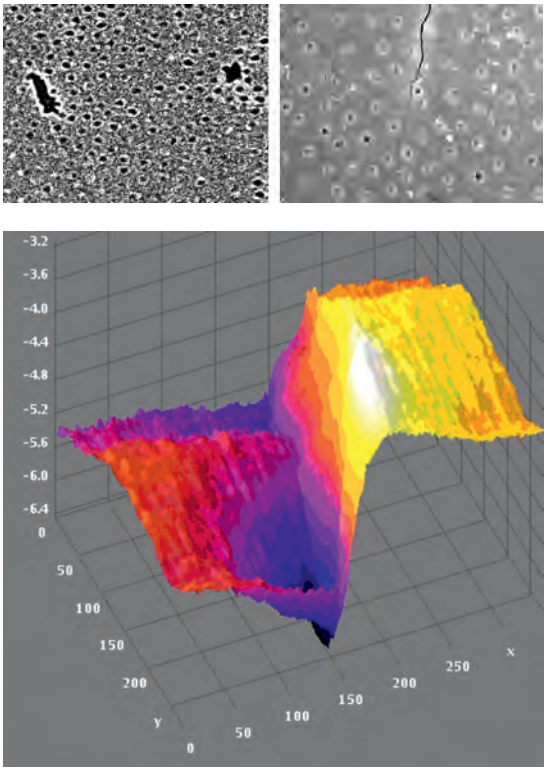

Fig 5: Phase-enhanced tomography slice in wet dentine (top left). Comparable information to that obtained by wet-mode SEM images of tubules with crack advancing under load (top right). Sequences of such images, combined with contrast-matching & statistical mage processing (wavelet-transform filtering) reveal nanometer displacement gradients increasing at and ahead of the crack tip seen in pseudo-3D displacement-magnitude profiles (bottom). Intertubular distance ~10 µm

Based on phase enhanced x-ray imaging (radiography) of dentine **[13]**, we are now able to resolve and find the spatial relationship between deforming zones in the tooth. As seen in **Fig. 5**, dentine tubules may be observed and tracked in slices in tomograms with submicron details (top left). This we hope to compare with environmental scanning electron microscope experiments of deforming and cracking wet dentine (top right). High resolution image-correlation analysis of images of the crack as it grows (bottom) reveal that the deformation process is non-linear, possibly due to the plasticizing effect of water.

To try and understand the extent to which water is involved in the deformation of teeth, neutron radiography and tomography contrast differences are being studied **(Fig. 6)**. Images of teeth immersed in D2O were compared with those of teeth immersed in deuterated methanol. Although limited by the moderate (supra-micron) resolution, preliminary results indicate that the deformation of the crown is constrained during the exchange of liquids. Tubules might be important for this. An asymmetric difference is seen in the right of **Fig. 6**, when tomograms of dehydrated teeth are subtracted from those of hydrated teeth, indicating that a difference exists in the contrast and scattering density of dehydrated roots. An asymmetric distribution of water around the root may be important for the mechanical functioning of the whole tooth.

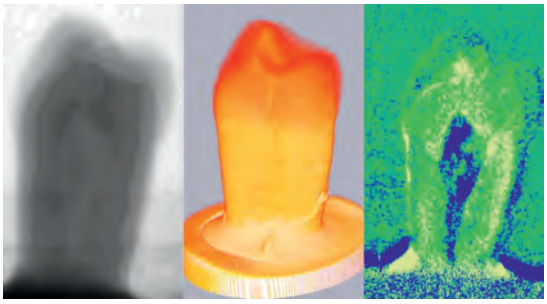

Fig. 6: Neutron radiography (left) and reconstructed tomography (centre) may be used to directly visualize the changes in contrast due to exchange of D2O and MethD4. Differential image (right) produced by numerical subtraction, shows bright yellow areas where water attenuation values were higher in the 'wet' state as compared with dark green and blue areas where attenuation is higher in the dry state. Much of the asymmetric difference is seen in the root section of the tooth.

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From Plant Cell Walls to Bio-inspired Composites

Plant cell walls are nanocomposites of cellulose microfibrils embedded in matrix polymers (pectins, hemicelluloses and lignin). As a result of adaptation to the different functional demands of plants, the cell wall polymers are arranged in many different patterns. The diversity in plant cell wall polymers and in their arrangement (cellulose microfibril orientation) results in biomaterials with very different properties. Thus investigating these "tuning parameters" is of importance to understand structure-function relationships and to learn from the broad range of nature´s plant cell walls. Confocal Raman microscopy (CRM) gives in situ insights into cell wall polymer composition and orientation with a high spatial resolution (<0.5 µm). The Raman imaging technique was during the last years successfully applied on different plant sources to reveal polymer compositions and orientations **[14-18] (Fig. 7)**.

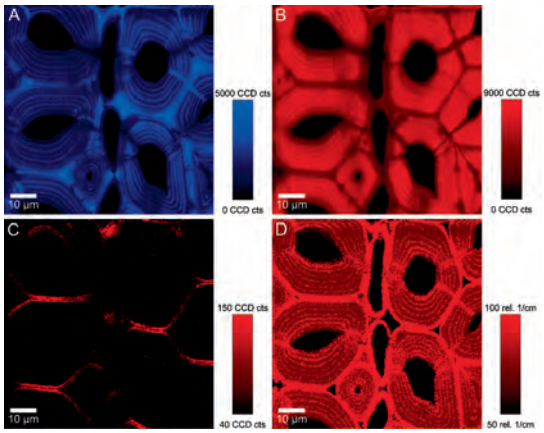

Fig. 7: Lignin distribution in the tropical tension wood (Laetia procera) shown by integrating from 1545-1698 cm-1 (A). Changes in cellulose amount and orientation visualised by integrating from 2774-3026 cm-1 (B), 1067-1106 cm-1 (C) and by plotting changes in band width from 2773-3044 (D)

Besides investigating the native cell wall, changes during tensile deformation **[19]** and enzymatic treatment **[20]** are of interest and can be followed by spectroscopic techniques. The development of a special designed fluidic cell by M. Schmitt, (Universität Heidelberg, in collaboration with Tillmann Rogge, Forschungszentrum Karlsruhe) allowed acquiring infrared spectra of biological samples in the wet stage and at controlled temperature as well as to exchange solutes. This enabled to follow for example in-situ the enzymatic degradation of the cellulosic G-layer in tension wood **[20]**.

Another approach is to build up cellulose nanocomposites by combining cellulose whiskers with different cell wall polymers and aiming to achieve preferred orientation for the cellulose whiskers **(Fig. 8)**.

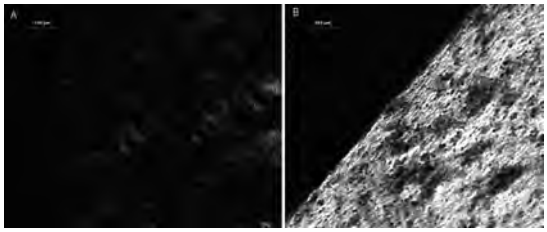

Fig. 8: Change in intensity of a light microscopic polarisation image (A) by rotating the sample 45°(B) as a hint for a preferred orientation in a cellulose/xyloglucan film.

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Biogenic Minerals and Bio-Inspired Nano-Composites

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Biological macromolecules play an important role in controlling the structure of biogenic minerals. Crystal size, shape and arrangement are modified by self-assembled organic matrices as well as soluble proteins. The resulting organic-inorganic composite structures have remarkable properties and hence constitute a rich source of inspiring concepts for the development of biomimetic materials. Besides hydroxyapatite, which is found in mammalian bone and teeth, calcium carbonate is a widespread biomineral that occurs in many marine invertebrates.

Biogenic and Biomimetic Calcium Carbonate

Biogenic calcium carbonate is of particular interest since it does not only cover a range of different morphologies, but also occurs in different polymorphs. Moreover, even the lattice parameters of biogenic calcite and aragonite were found to be anisotropically distorted, presumably due to the presence of intracrystalline proteins **[1]**.

Our research focused on studying the structure of intracrystalline organic inclusions with the aim of explaining differences between biogenic and geological calcite. In cooperation with E. Zolotoyabko (Technion, Haifa, IL) we investigated prismatic calcite crystals **(Fig. 1)** that were extracted from the shell of Pinna nobilis.

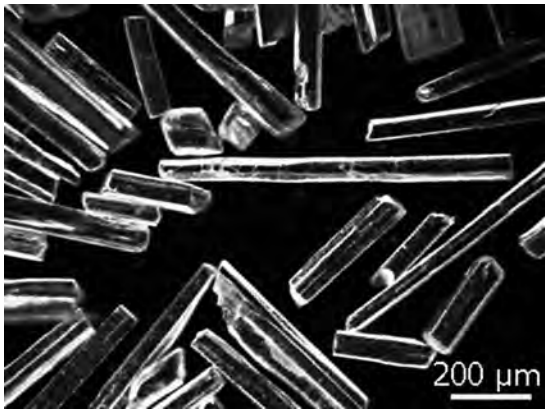

Fig. 1: Dark field light microscopy image of prismatic calcite crystals from a mollusk shell (Pinna nobilis).

Using a new experimental setup that was developed together with the group of O. Paris (Biomaterials Dept.) allowed for simultaneously studying the wide- and small-angle X-ray scattering behavior of single biogenic calcite crystals with a microfocus synchrotron beam at BESSY II (Berlin). **Fig. 2** shows an example for a 2-dimensional scattering pattern. The spots correspond to a single crystalline diffraction pattern of calcite. The small-angle scattering visible in the center, which arises from the organic inclusions, is anisotropic. As can be seen in the inset, which shows the small-angle region (000) in higher magnification, this anisotropy correlates with the crystallographic orientation.

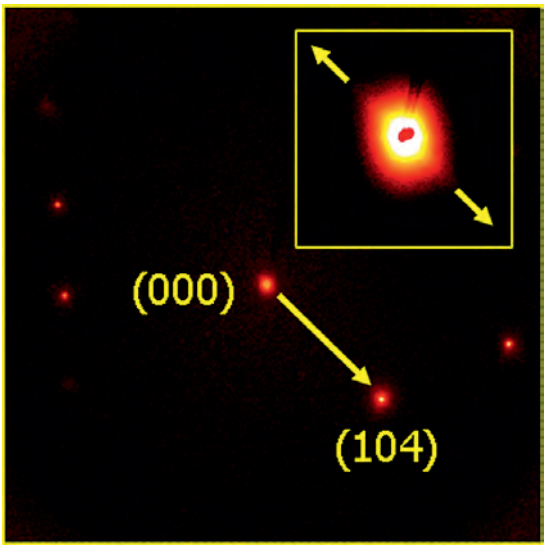

Fig. 2: Scattering of a single biogenic calcite crystal (Pinna nobilis). The anisotropic small-angle scattering (000) points towards the (104) orientation. The inset shows a higher magnification of the small-angle region.

A more detailed analysis showed that the organic inclusions are preferentially oriented not only along the {104} but also along the {001} crystallographic planes. Furthermore the small-angle scattering studies gave proof of the presence of a very rough internal interface between the organic inclusions and the surrounding mineral lattice. We assume that this large amount of interface is of major importance for controlling the properties of the biogenic mineral crystals.

Inspired by our findings on the structure of biogenic calcite, we performed similar investigations on biomimetic calcite that was precipitated in the presence of a soluble polymeric additive (in cooperation with H. Cölfen, Colloid Chemistry Dept.). Polystyrenesulfonate (PSS) was previously shown to induce the formation of calcite mesocrystals which consist of aligned nanocrystalline building blocks **[2]**.

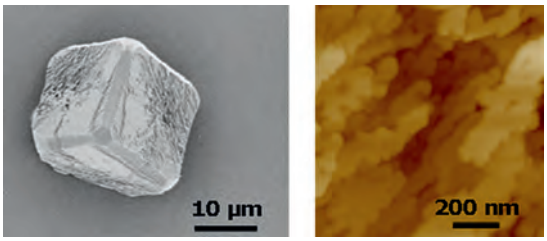

Fig. 3: SEM (left) and AFM image (right) of a calcite-PSS composite particle. The rounded corners of the particle belong to exposed {001} planes. The roughness of the surface can be seen in higher magnification in the AFM image.

The effect of the polymer on the morphology and the rough outer surface of the particles are shown in **Fig. 3**. The interaction with the polyelectrolyte favors the exposure of the charged {001} surfaces which appear additionally to the usually exposed low-energy {104} surfaces.

The characterization of these composite particles by means of X-ray scattering revealed several interesting structural features resembling the characteristics of biogenic calcite. The calcite-PSS particles appeared to be single-crystalline with polymer inclusions that are preferentially oriented, mainly along the {104} crystallographic planes **(Fig. 4)**. Moreover, the particles were also found to have a large amount of rough interface between the polymer and the mineral. This interface could be used to tune the properties of such composite particles.

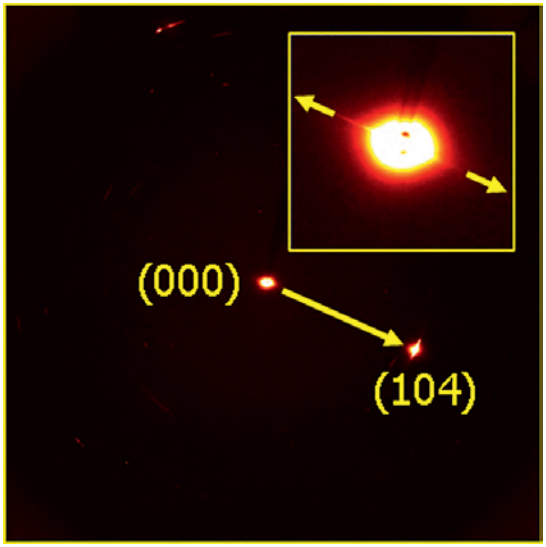

Fig. 4: Scattering of a single-crystalline calcite-PSS composite particle. The inset shows a higher magnification of the small-angle signal which points towards the (104) orientation.

The research was complemented by additional studies on Mg rich calcite from the tip of sea urchin teeth, together with Y. Ma and her coworkers from the Weizmann Institute of Science (Rehovot, IL). Specifically, the effect of Mg gradients and crystal orientations on the grinding capabilities and self-sharpening of the tooth were investigated **[3]**.

In the future, we will extend our research interests towards the development of biomimetic organic-inorganic composites with well controlled interfaces allowing for the combination of high stiffness with high toughness. Another aim will be to study the role of proteins for the formation of amorphous calcium carbonate in crayfish gastroliths (cooperation with A. Berman, BGU, Beer-Sheva, IL).

Mineralization of Tooth Enamel

Amelogenin proteins are the main component of the developing enamel tissue during its early stage of formation. In previous investigations **[4]** we analyzed the formation of so-called amelogenin "nanospheres" and showed an onset of their aggregation. This aggregation presumably leads to the formation of amelogenin chains that guide the growth of hydroxyapatite crystals during enamel mineralization.

Continuing these studies on the recombinant amelogenins rP172 and rM179 in cooperation with H. Margolis et al. (The Forsyth Institute, Boston, USA) **[5]**, we obtained more detailed information on the shape of the amelogenin nanoparticles which turned out to be oblates with an aspect ratio of 0.45. This was concluded from small-angle scattering measurements of protein suspensions **(Fig. 5)**.

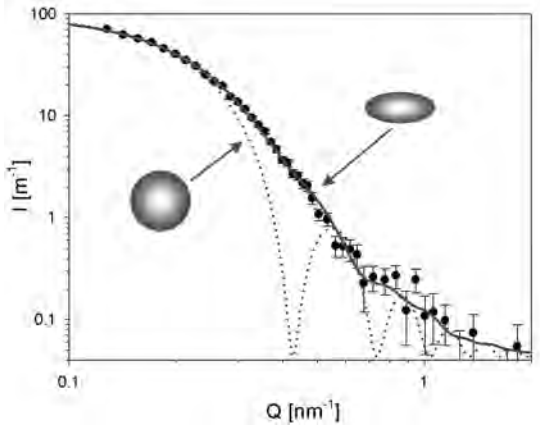

Fig. 5: Small-angle scattering profile (Intensity I vs. modulus of the scattering vector Q) of the recombinant amelogenin rP172 at pH8.1 and 4°C. The scattering is not consistent with monodisperse spheres (grey dotted line) but can be very well described by oblates (grey line).

The observed anisometric shape must be of crucial importance for the directed aggregation of the amelogenin particles into chain-like structures. Moreover, pH and temperature dependent measurements in different buffer solutions gave proof that the aggregation of (recombinant) amelogenin oblates occurs at a pH value of 7.2 which is close to physiological conditions.

Future studies will focus on the self-assembly behaviour of native amelogenins in order to evaluate the relevance of our results for the in-vivo formation of enamel.

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Mesoscale Materials and Synchrotron Research

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The research group has continued work on three different topics: 1) Further development and operation of the experimental station for simultaneous microbeam small- and wide-angle scattering (SAXS/WAXS) at the microfocus (µ-Spot) beamline at BESSY in BerlinAdlershof. 2) The comprehensive structural characterization of several biological materials which serve as inspiration source for biomimetic materials, and the attempt to transform some of them into potentially useful ceramics by combined thermochemical approaches. 3) The study of fluids in ordered mesoporous silica, with particular emphasis on the elastic deformation of the pore walls by the sorption and capillary condensation of the fluid. Much of the experimental work performed in 2) and 3) is based on position resolved and/or in-situ X-ray scattering at the BESSY instrument.

1) µ-Spot Beamline at BESSY

The SAXS/WAXS instrument at the BESSY µ-Spot beamline is fully operational since mid 2006 **[1]**. More than 40 experiments where conducted since then by user groups from the Biomaterials Department including some external cooperation partners. They were in all cases technically and in most cases also scientifically supported by our group. Some of the experiments will be described in more detail in the corresponding reports of other research groups or independent researchers from the department (Aichmayer, Burgert, Faivre, Gupta, Zaslansky), and only a short summary is given in the following. Microbeam scanning SAXS/WAXS is one of the most successful options of the BESSY instrument, allowing to construct maps of nanostructural parameters extracted from the SAXS/WAXS patterns with a resolution in the micrometer regime **[2]**. Examples of recent experiments on different types of biological materials include crustacean cuticles **(Fig. 1)**, plant cell walls, bone, and teeth.

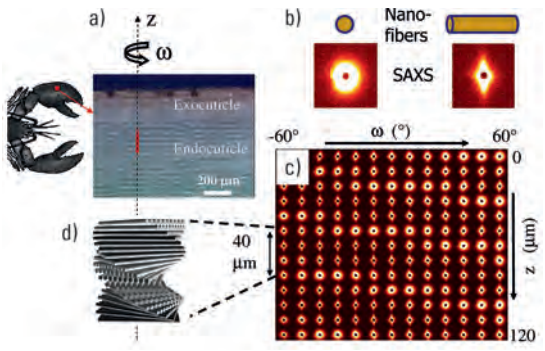

Fig. 1: 2D SAXS mapping of lobster cuticle nanostructure. a) Online light microscopy image of the specimen. b) SAXS patterns from chitin nanofibrils and their relation with fiber orientation. c) Composite image of SAXS patterns (10 µm beam) as a function of sample rotation angle ω and vertical sample position z. d) The characteristic change of the anisotropy of the SAXS patterns directly visualizes the rotated plywood structure of the chitin nanofibrils

Successful scanning SAXS/WAXS experiments were also conducted with external cooperation partners on sea urchin tooth (Weizmann Institute, Israel) and insect mandibles (Drexel University, Philadelpia). In close cooperation with the group of B. Aichmayer we have furthermore developed microbeam single crystal diffractometry combined with simultaneous 3D-SAXS. Here, the combination of microbeam SAXS/WAXS with full sample rotation is used for 3D reciprocal-space investigation of single crystalline or strongly textured particles of only a few microns size. Recent applications include single calcite particles of biogenic (cooperation: Technion, Haifa, Israel) and synthetic origin (cooperation Cölfen group, Colloid Chemistry) **[3]**, and on calcium phosphate particles (cooperation: Taubert group, Colloid Chemistry).

In-situ SAXS/WAXS are the second large group of experiments conducted at the BESSY instrument. Special devices have been developed and used for in-situ fluid sorption in mesoporous materials, for in-situ mechanical experiments on bone and other biological tissues, and for combined in-situ mechanical deformation and humidity control of plants. First approaches to combine in-situ experiments with microbeam scanning SAXS/WAXS have also been initiated by in-situ sample heating, combined with microbeam scanning of lobster cuticle (see below). Moreover, a first successful in-situ bending experiment combined with scanning from the tensile to the compression side of a lobster cuticle cross section was also conducted recently. Another in-situ experiment investigated mechanical creep of single carbon fibers of 10 µm diameter at high temperature (up to 2000°C) in cooperation with the University of Vienna.

2) Biological Materials and Biomimetic Processing

Crustaceans are known as the kings of mineral mobilization in the animal world. The crustacean cuticle is a nanocomposite consisting of chitin nanofibers associated with proteins and minerals, the latter being either calcite or amorphous calcium carbonate (ACC). The highly sophisticated hierarchical structure of the cuticle makes it an optimized material for mechanical protection and calcium storage. We have investigated the local nanostructure of lobster cuticle with scanning SAXS/WAXS, and have described the complex texture of the chitin fibers, as well as the crystallographic orientation relationship between chitin and the calcite mineral **[4]**. Moreover, we have shown that this calcite phase in lobster cuticle is restricted to a thin layer at the outermost exocuticle, while the rest of the cuticle contains exclusively ACC. We have attributed the function of the calcite layer to a mechanical protection role, in particular with respect to impact and wear resistance **[4]**. In a successive in-situ heating experiment we could show that the ACC phase transforms to calcite above 400°C, i.e. at a temperature exceeding the one of the biopolymer degradation by far **(Fig. 2)**. This allows speculating about the stabilization mechanisms of amorphous minerals, which is presently one of the key-questions in biomineralisation.

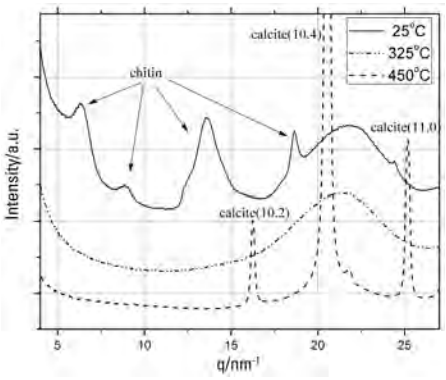

Fig. 2: WAXS profiles from lobster endocuticle as a function of temperature (taken from [4]). At 325°C, the crystalline chitin has fully decomposed and only a broad hump from ACC remains. At 450°C, almost all the amorphous mineral has been transformed into calcite.

Silica is one of the most abundant biominerals on earth besides calcium carbonate and calcium phosphate. In certain plants such as in rice husks for instance, considerable amounts of amorphous silica can be found in the outer epidermis. The functional role of silica in plants is however not yet clear. We have studied the structure of the perennial plant Equisetum hyemale (horsetail or scouring rush) with a series of complementary analytical techniques **[5]**. We could show that besides the known silica accumulations in particular knobs, the whole epidermis is covered by a thin silica layer. We attributed this to a mechanical protection role of silica for the plant body.

Besides the structural characterization, we have also attempted to isolate the biogenic silica from Equisetum hyemale **[6]**. Several chemical and thermal treatments were employed, and the structure and quality of the observed silica material was investigated by nitrogen sorption and small-angle X-ray scattering. Both, the long term treatment with hydrogen peroxide **(Fig. 3)** as well as short term treatment with hydrochloric acid followed by calcination revealed high quality mesoporous silica with large surface area (up to 400 m^2/g). Moreover, the macroscopic shape of the plant stalk could be perfectly preserved by the treatment **(Fig. 3)**. Therefore, this work opens new prospects for the production of high grade micro- and mesoporous silica from renewable resources.

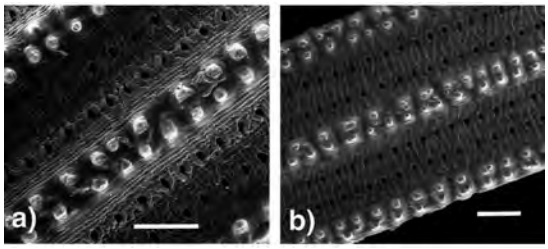

Fig. 3: Scanning electron micrographs of a native (a) and a long-term H_2O_2 treated sample of Equisetum hyemale (b). The sample in (b) consists of pure silica (taken from [6]). The length of the bars is 300 µm.

3) Fluids in Mesopores

In the framework of the Collaborative Research Center Sfb 448 "Mesoscopically Organized Composites", we have continued our work on in-situ sorption of fluids in ordered mesoporous silica using X-ray and neutron scattering. Moreover the development of simple physical models to describe the pore structure and the sorption process was also initiated. We have concentrated in particular on the deformation of the solid pore walls of the silica matrix during fluid sorption and condensation. These sorption strains can simply be obtained from the shift of the Bragg peaks from the ordered pore matrix in the used mesoporous materials SBA-15 and MCM41. The dependence of the strain on the fluid pressure at constant temperature ("sorption isotherm"), **Fig. 4** shows a continuous expansion during sorption, interrupted by a sudden contraction at capillary condensation. This behavior can be qualitatively understood by continuum thermodynamic and mechanical arguments **[7]**. Moreover numerical simulations performed by our cooperation partner from the TU Berlin show good agreement with the experimental data **[7]**.

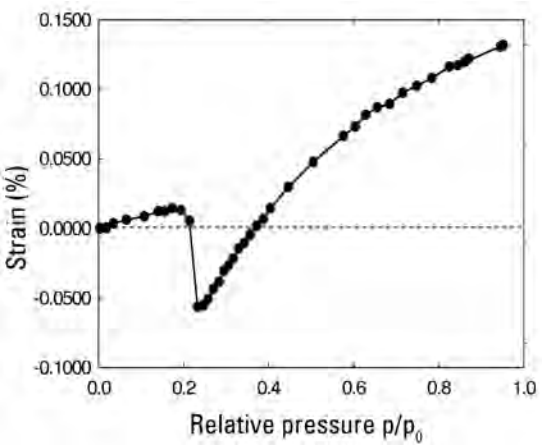

Fig. 4: Pore lattice strain of MCM-41 silica as a function of relative pressure of pentane at room temperature.

Strain isotherms as shown in **Fig. 4** were measured for different materials, for different pore diameters, and for different fluids. These data allow developing and refining sophisticated structural and mechanical models for these materials and lead to a better understanding of fluid-solid interactions in confined geometry. In addition, nanoelastic properties of the investigated materials can be estimated from these data in a unique way, which might be of great value for many novel mesoporous materials.

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→ Heterophase Polymerization
→ Biomimetic Mineralization and Crystal Growth Control
→ Chimera Polymers and Novel Polymerization Techniques
→ Modern Techniques of Colloid Analysis
→ Materials for Energy Applications
→ Hydrothermal Carbon Nanostructures and Coatings
→ De Novo Nanoparticles
→ International Joint Laboratory

COLLOID CHEMISTRY

Research in the Department of Colloid Chemistry

Scientific Profile

The size of the Department of Colloid Chemistry is currently about 60 people, with many independent researchers covering a wide range of research topics. The effective constituting element of the scientific activities is the "project", structure headed by a senior scientist involving a mixture of technicians, graduate students and post-docs (3-8 people). Projects are related to scientists, but have a temporal character of usually about 5 years. After this time, permanent scientists have to redefine their profile to justify the allocation of resources. In the case of non-permanent scientists, the projects usually leave the department with the promotion of the scientist, i.e. the group leaders can continue their specific research in their new academic environment (usually as professors) without competition of the former group.

In the time of this report and after a "drain" of 4 group leaders in the period ahead, reconstruction of the department went on and was most serious. Dr. Arne Thomas, head of the ENERCHEM project is in the process of leaving the institute towards a full professorship (TU Berlin), and the Emily Noether group of Dr. Hans Börner is also developing towards a professorship. The new group of Dr. Maria Magdalena Titirici on "Hydrothermal Carbon" was complemented in October 2008 by two other new groups, Dr. Cristina Giordano ("De Novo Nanoparticles"), and Dr. Xinchen Wang ("Artificial Photosynthesis"), who however are mainly involved in build-up operations. This turnover is beyond typical and not easy, but reflects the dynamic character of the department.

The profile of the department has therefore been seriously reoriented, keeping only some of the old strongholds. The following topics are treated by the department:

- Heterophase Polymerization
- Biomimetic Mineralization and Crystal Growth Control
- Chimera Polymers and Novel Polymerization Techniques
- Modern Techniques of Colloid Analysis
- Materials for Energy applications
- Hydrothermal Carbon Nanostructures and Coating
- New inorganic nanoparticles
- Artificial photosynthesis

These projects within these project groups are briefly explained below:

Heterophase Polymerization

The notation "Heterophase Polymerization" summarizes the techniques of suspension-, emulsion-, mini-, and microemulsion-polymerization as well as precipitation polymerization. The solvent is usually water, but heterophase polymerization in inverse media is also examined. This class of techniques, although more than 90 years old, experiences a strong renaissance, since it allows the production of high polymer containing formulations in water as an environment-friendly solvent.

Central points of interest of the team working on heterophase polymerization are:

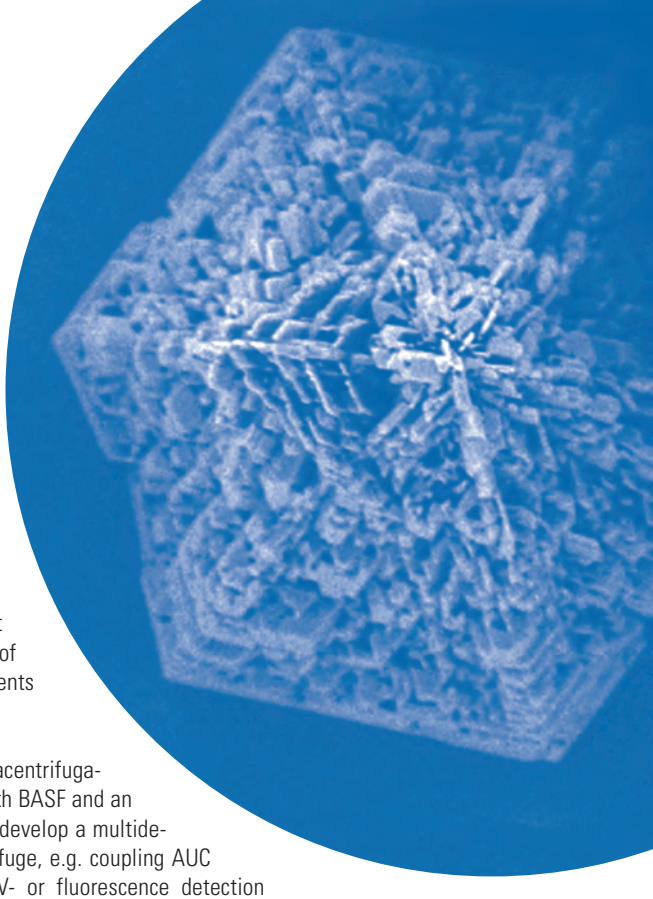
- We want to gain a better understanding of the nucleation period and particle formation for an optimal control of the particle size and polydispersity. For this purpose, new experimental online multidetection techniques are developed; the experimental investigations are supplemented by theoretical and numerical descriptions *(Dr. Klaus Tauer)*.

- We want to simplify the synthesis of complex polymer morphologies on a molecular level (synthesis of block & graft copolymers by emulsion polymerization) and on a colloidal level (core-shell latices, hollow spheres, one-step synthesis of reinforced materials) by a rational use of the particle interfaces in heterophase polymerization *(Dr. Klaus Tauer)*.

Biomimetic Mineralization and Crystal Growth Control

Polymers can step in the precipitation of inorganic and organic molecules and control the growth of the nucleated particle. Here, we are mainly (but not exclusively) interested in so-called double-hydrophilic block copolymers where one block mediates water solubility, whereas the other interacts with the surface of inorganic or polar organic particles.

- The solution structures of diverse minerals prior to crystallization are analyzed by on-line multidetection techniques. It turns out that the classical picture of nucleation is by far too simple could be redefined by inclusion of a whole set of different amorphous species *(Dr. Helmut Cölfen)*.



- The tectonic arrangement of nanoparticles can be controlled by the spontaneous action of polymers and allows, analogous to the model of bone or seashell, the construction of superior hybrid materials *(Dr. Helmut Cölfen, together with the Biomaterials Department)*.

- These principles also enable the colloidal formulation of organic drugs and pigments *(Dr. Helmut Cölfen)*. The origins of supramolecular chirality are analyzed.

Chimera Polymers and Novel Polymerization Techniques

Amphiphilic polymers consist of components which dissolve in different media, e.g. a hydrophilic and a hydrophobic part. Since we are able to adjust both components sensitively to the dispersion medium as well as to the dispersant, amphiphilic polymers allow the stabilization of unusual dispersion problems. Recently, we learned that very special effects, not only for biological interfaces, can be addressed when one block is a biopolymer, whereas the other mediates to the "technical world" (Chimera Polymers). Focal points of interest in this range are:

- The micelle formation and lyotropic liquid crystalline phase behavior of chimera polymers is examined in dependence of the molecular structure, the relative amount of the different components, as well as the secondary interactions between the structure forming bio-like blocks *(Dr. Helmut Schlaad)*.

- The introduction of secondary interactions such as H-bridges, dipole interactions or metal-ligand binding results in superstructures with more complex order and broken symmetry *(Dr. Helmut Schlaad)*.

- The performance of molecular drugs can be highly enhanced or optimized by coupling to a colloidal system with synergistic action. Here, our specific knowledge on the synthesis and physical behavior of functional polymers and colloids is used in cooperation with pharmaceutical/medical partners to generate tailor made colloidal drug carriers and diagnostica *(Dr. Hans Börner/ Dr. Helmut Schlaad)*.

Modern Techniques of Colloid Analysis

All the work described above is necessarily accompanied by a considerable amount of colloid analysis which includes fully commercial techniques, but also relies on the development of new techniques or methods of data handling. The developments in this area include:

- The development of new ultracentrifugation techniques. Together with BASF and an American partner group, we develop a multidetection kit for the ultracentrifuge, e.g. coupling AUC separation with Raman-, UV- or fluorescence detection which allows an in-situ chemical analysis within a separating complex colloidal mixture. By opening a bunch of new possible scientific applications, we intend to revitalize the AUC. *(Dr. Helmut Cölfen, Project "Open AUC" together with the BASF AG)*.

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

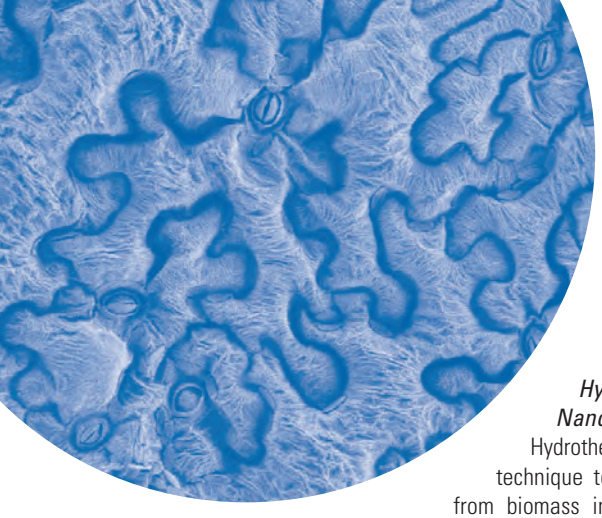
Materials for Energy Applications

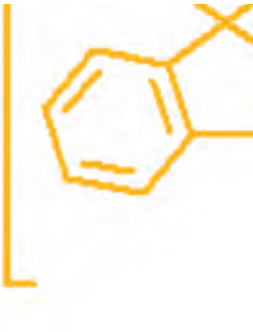
The Max Planck Society has established a new instrument to improve the impact and visibility of basic science for society, so-called project clusters or project houses. The first of these project houses to come into existence was ENERCHEM, devoted to the materials chemistry to handle energy problems. This project house was initiated by the Inorganic Chemistry Department of the Fritz Haber Institute and the Colloid Chemistry Department and is coordinated by Markus Antonietti.

Hydrogen storage, better fuel cells, new energy cycles, new catalysts for more efficient processes, methane activation, better batteries, ultracapacitors, remote energy storage, lightweight solar cells, all these topics are intimately connected with the control and design of materials nanostructure. Activities based in Golm include:

- New C/N-polymers and carbon materials to expand the property profile of carbon *(Markus Antonietti)*

- Porous tectonic polymers as membranes for fuel cells and battery separators and as novel gas storage materials *(Dr. Arne Thomas, on the leave)*





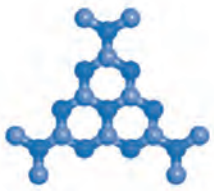
Hydrothermal Carbon Nanostructures and Coatings

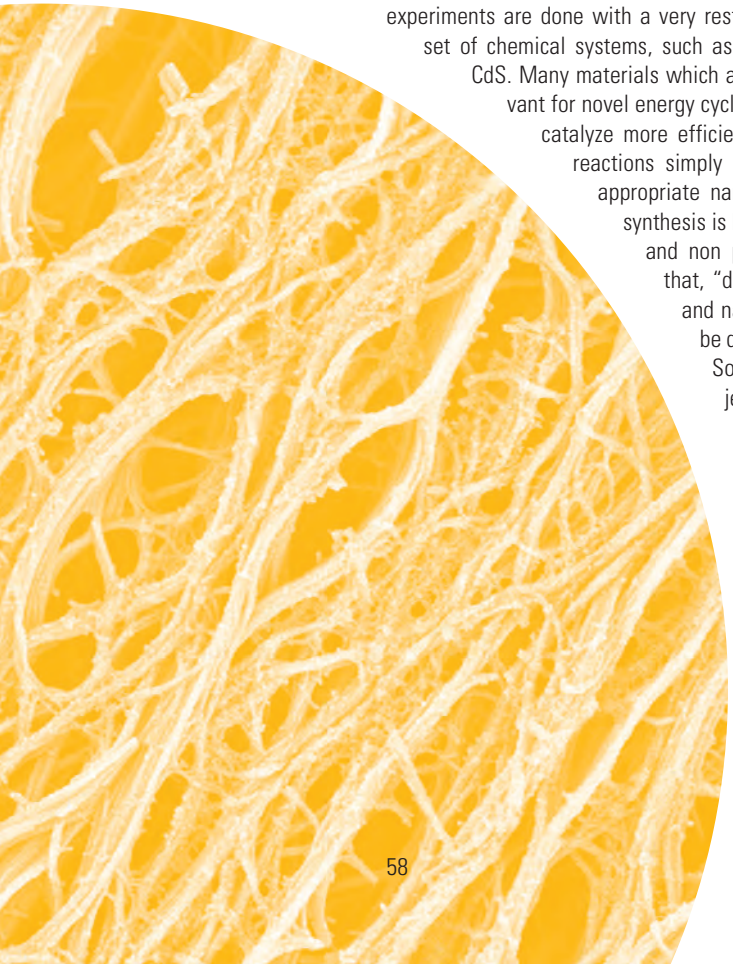
Hydrothermal Carbonization is a 100 year old technique to generate carbonaceous materials from biomass in a colloidal heterophase reaction processes. We reactivated this process to address questions of the sustainable/chemical synthesis of carbon nanostructures and the climate change. First experiments indicate that not only the non-oil based raw material base ("sugar") is highly attractive; it is also that a multiplicity of appealing carbon nanostructures can be addresses with great ease and high potential:

- HTC of raw biomass to generate soil conditioner ("black soil") and its interaction with the microbial biosystem *(Markus Antonietti, Maria Magdalena Titirici, together with the MPI of Biogeochemistry)*
- Analysis of the elemental chemical steps of HTC and hybridization with technical monomers to generate new filler structures *(Dr. Maria Magdalena Titirici)*
- HTC reaction to coat nanoparticles and mesoporous scaffolds for catalysis, battery applications and modern chromatography *(Dr. Maria Magdalena Titirici).*

De Novo Nanoparticles

In spite of the fact that nanoscience is not exactly a new discipline, anymore, it is astonishing that the width of easily accessible nanostructures is still rather small, i.e. most experiments are done with a very restricted set of chemical systems, such as Au or CdS. Many materials which are relevant for novel energy cycles and to catalyze more efficient chemical reactions simply do not exist as appropriate nanostructures, or their synthesis is highly not sustainable and non practical. Because of that, "de novo" nanosystems and nanosyntheses have to be designed from scratch. Some cases of the project portfolio are:





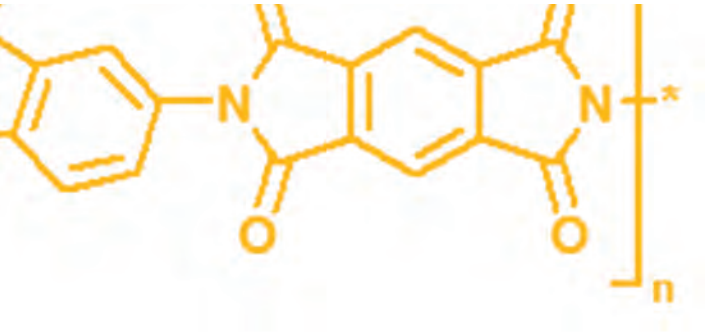
- Metal carbide and nitride particles offer new pathways for metal/base catalysis, but also are record holders in mechanical hardness or magnetization *(Dr. Cristina Giordano).*
- This is also true for the corresponding metal borides an bronnitrides, which are new land for chemistry, when rational nanostructures are to be made (Dr. David Portehault (CNRS SuperPostDoc program, together with Dr. Cristina Giordano).
- New cathode nanomaterials for the lithium batteries are another target where progress will directly impact society. Here, doping, superstructure formation and conductive coatings are additional issues to be addressed within synthetic protocols *(Dr. Cristina Giordano).*

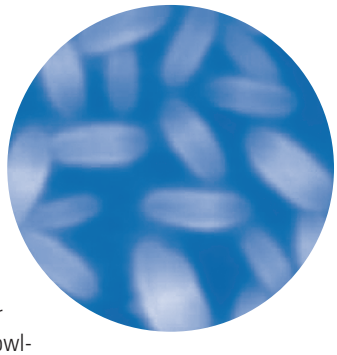
Synthesis development in this group is always accompanied with the suitable physical characterization techniques. This includes, among others, high-resolution TEM microscopy, scattering techniques and magnetic characterization.

Artifical Photosynthesis

This international joint laboratory was established in July 2008 between the Max-Planck Institute of Colloids and Interfaces and Fuzhou University. It is intended to establish international research collaboration for artificial photosynthesis which are planned to be extended the next period.

Natural photosynthesis, the process by which green plants are converting solar energy into chemical energy, has inspired the development of artificial versions of photosynthesis, i.e. (1) the splitting of water into hydrogen and oxygen, and (2) the conversion of carbon dioxide into organics via sunlight. An important challenge in artificial photosynthesis is the development of catalysts that should be sufficiently efficient, stable, inexpensive, and capable of harvesting the abundant visible light in solar spectrum. There are countless trials to establish stable systems for this purpose, mostly based on inorganic semiconductors with appropriately engineered band-gap and noble metals to promote the "extraction" of electrons. These materials include metal oxides, (oxy)sulfides, and (oxy)nitrides. This group investigates polymeric and organic-inorganic hybrid materials with controlled nanostructures as potential energy transducers for artificial photosynthesis. Potential applications include solar energy conversion, environmental purification, and organic synthesis. *(Dr. Xinchen Wang)*





Visions and Future Perspectives for the Next Years

The group is continuing its way from a phase of being diversified in many junior projects to a period with more coordinated research and longer term goals.

As the TU Berlin has established a National Excellence Centre on Catalysis, it is a clear intention to further improve the cooperation with those colleagues, and a set of larger funding applications has been placed, thus hopefully allowing feed this interface with developed young persons. First scientific results from this cooperation are very promising.

The started projects on "Energy Materials" and "Processes for the Raw Material Change" turned out to be very timely and secured the department in the last four years clear visibility a leading European role in these activities. It is my personal intention to expand these activities.

Partly driven by the colloid department, but also by the other departments, we progress with the internationalization of our relations. Beside the well established Partner group at USCT/Hefei, we will enter a virtual "Artifical Photosynthesis Center" with the University of Fuzhou and Tokio University, become European Partner Group of the Iberian Center for Nanotechnology, and establish an Exchange Program with Kyushu University (together with Department of Interfaces).

Relations to Industry and Society

The department is involved in a large number of industrial projects. We promote fruitful and truly mutual relations with BASF AG, Firmenich, and Merck. These operations include scientific cooperation, knowledge exchange, consulting, the solution of minor scientific problems or measurements, and knowledge transfer to create the scientific base for products of the companies.

I am a board member of 15 scientific journals, and I consult the Royal Society of Chemistry/UK in questions of international exchange and benchmarking. In science policy, I regularly act as a referee in DFG, European and International science evaluations. I am a board member of the ERACHEM defining the future tasks of chemistry on the European level. I regularly go to schools and lecture about the problems of a developing society and how to respond on the base of scientific knowledge and education. In 2008, I received the ERC Senior Excellence grant for our colloid activities in sustainable chemistry. In 2009, I will receive the Polymer Medal of the UK Polymer group, which is a distinction for lifetime achievements.

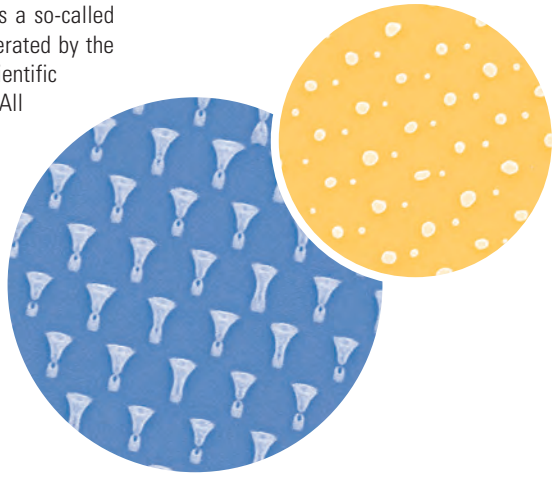
Markus Antonietti,
Director of the Department
of Colloid Chemistry

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,
- chromatographic lab including a number of modern chromatography techniques,
- reaction calorimetry with online multidetection,
- analytical and preparative ultracentrifugation,
- thermal analysis, DSC and porosimetry,
- MALDI-TOF-mass spectrometry,
- FT-ATIR for liquid analysis.

One of the labs, the electron microscopy lab, is a so-called "central service labs", i.e. it belongs and is operated by the department, but is also designated to perform scientific routine measurements for the whole institute. All other instrumental labs are not devoted to service operations, but are nevertheless heavily involved in inter-department projects.



Polymer Dispersions/Heterophase Polymerizations

Klaus Tauer 27.09.1951
1974: Diploma, 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 poly(arylene vinylene) polymers
1977-1991: Scientific Coworker Institute of Polymer Chemistry of the Academy of Sciences of the GDR in Teltow-Seehof
Since 1992: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2004: "Privatdozent" Polymer Colloids, University of Potsdam

Spontaneous Emulsification

A closer look at the oil – water interface in the absence of any external shear reveals that droplets being created spontaneously on either side immediately after contacting two immiscible liquids **(Fig. 1)** **[1, 2]**. Freely moving oil drops in the water phase have been observed for polar oils but also for non-polar oils. The water drops do not move but adhere to the glass walls of the observation cell and the shape of larger ones is non-spherical.

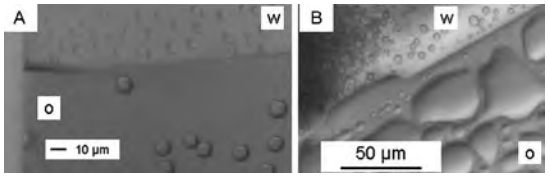


Fig. 1: Light microscopy images showing droplet formation on either side of the interface between A: chloroform – water and B: cyclodecane – water; o and w denotes the oil and water phase, respectively.

These experimental findings are crucial for developing the foundations of a consistent mechanism of heterophase polymerization (monomers are oils) and open new ways to modify latex particles.

Consistent Mechanism of Emulsion Polymerization

Spontaneous emulsification strongly influences both particle nucleation and swelling of particles **[3, 4]**. In the presence of monomer drops nucleation is for styrene EP heterogeneous in nature as illustrated by the TEM images of **Fig. 2**.

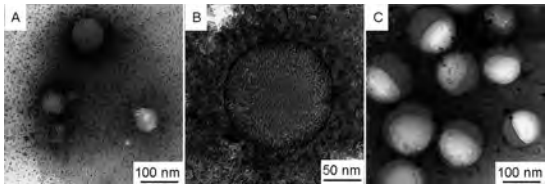


Fig. 2: TEM images illustrating the deposition of oligomeric particles onto styrene droplets during the early stage of unstirred emulsion polymerization; A: t_{equ}=5 min after 40 minutes polymerization time, B: t_{equ}=120 min after 30 minutes polymerization time, C: t_{equ}=180 min after 30 minutes polymerization time

Accordingly, particle nucleation (that is the precipitation of water-born oligomers) is enhanced by the droplet interface and particle morphology depends on the monomer equilibration time (t_{equ}).

This scenario explains all the experimental observations from spontaneous emulsification and formation of vesicular or hollow particles at high initiator (persulfate) concentration. If however, the polymerization conditions are changed resulting in nucleated particles made of oligomers with higher molecular weights, which are soluble in the droplets, solid particles are formed **(Fig. 3)**.

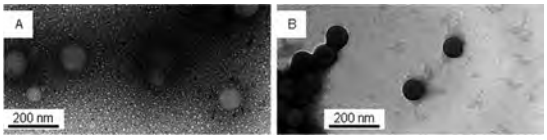


Fig. 3: TEM images of particles after polymerization time of 30 min for non-stirred surfactant-free emulsion polymerizations of styrene with 120 min monomer equilibration time; experimental conditions: all-glass reactor, 70 °C, 20 ml of styrene, 562.5 g of water, 1.25 g of KPS (A) and 0.094 g of KPS (B)

For more hydrophobic monomers such as *t*-butyl styrene the nucleation mechanism changes in dependence on initiator concentration. Droplet nucleation, that is, direct entry of radicals into monomer droplets, dominates at lower initiator concentrations.

Modification of Colloidal Particles

Colloidal polymer particles take up solvents without being dissolved. This swelling process is a complicated interplay between polymer and colloid chemistry and only poorly understood **[3, 4]**. Swelling takes place either via molecular diffusion of the swelling agent through the aqueous phase or via interaction with spontaneously formed droplets. In the latter case colloidal particles take up not only water insoluble materials but also substances with that they macroscopically only hardly interact. Exemplarily, polystyrene latex particles can be modified with poly(methyl methacrylate) **[3, 4]** or colloidal silica with paraffin wax **[5]**.

Multiscale Modeling of Heterophase Polymerization

EP is a highly complex dynamic process in which chemical and physical events simultaneously occur at very different time and length scales. In free-radical polymerizations reaction rates range from about 1 to 10^9 s^{-1} and involve ions and molecules (size < 1 nm), macromolecules (1 – 10 nm), polymer particles (10 nm - 1 µm) and monomer droplets (up to > 1 µm).

The averaging of classical deterministic modeling clearly has limitation especially for considering details of heterogeneous systems.

In the new multiscale modeling approach, different events are investigated at different time and length scales using suitable simulation methods such as Molecular Dynamics (MD) simulation, Brownian Dynamics (BD) simulation, and kinetic Monte Carlo (kMC) simulation. MD simulation is used to estimate the diffusion coefficients under the specific conditions. These diffusion coefficients are then used by the BD simulation method to describe the molecular motion at a much larger time and length scale. For instance, BD simulation is used to determine the rate of radical capture by polymer particles, **[6]** as well as the rate of radical desorption from the particles to the continuous phase **[7]**. Similarly, the BD method can be used to simulate monomer swelling dynamics **[8]**.

BD simulations are extremely useful to achieve a deeper understanding of radical entry into latex particles as a key step in EP kinetics. Models relying on the Smoluchowski equation are insufficient as it is valid for a single particle at infinite dilution but in reality the polymer volume fraction Φ_p can be well above 50 %. The numerical results **(Fig. 4)** show for a wide range of D (particle diameter) and N (particle number) that radical entry expressed by the Smoluchowski number depends linearly on Φ_p.

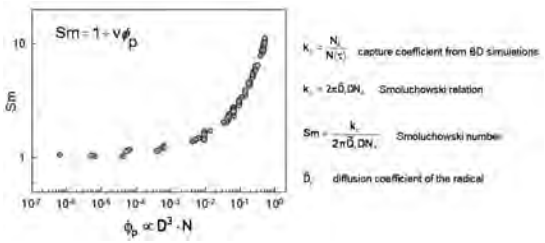


Fig. 4: Dependence of radical entry on Φ_p (BD simulations) [6]

Heterophase Polymerization as Synthetic Tool

Unique block copolymers are easily accessible by heterophase polymerization initiated with hydrophilic polymeric radicals **[9]**. This method relies on the fact that polymeric radicals can survive in isolated latex particles that are stabilized by hydrophilic blocks. The newly developed strategy of joint polymerization can be successfully applied to produce silica-containing block copolymer particles in a one-step procedure **[5]**. The hydrolytic condensation of the siloxanes takes place in the region of the block copolymer particles where the poly(N-isopropyl acrylamide) (PNIPAM) is located. This part is on the one hand hydrophobic enough to absorb the siloxanes and on the other hand it contains enough water to start hydrolytic condensation. The morphology of the SiO_2 that is obtained after calcination depends on the morphology and composition of the block copolymer particles **(Fig. 5)**. Triblock copolymers with PNIPAM middle blocks lead regardless of the nature of the hydrophilic precursor polymer to spherical silica particles. If however, the core of the block copolymer particles consists of a hydrophobic polymer the morphology of the silica after calcination changes completely as a macroscopic solid with nanopores is obtained.

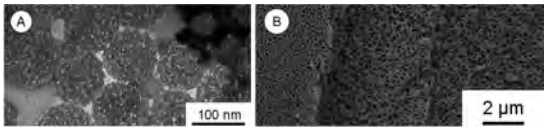


Fig. 5: TEM (A) and SEM (B) image of the silica obtained after calcination of various block copolymer particles; A: poly(styrene sulfonate)-PNIPAM-poly(vinyl trimethoxysilane) B: poly(ethylene glycol)-PNIPAM-poly(butyl acrylate)-poly(vinyl trimethoxysilane)

URT for Studying Phase Transitions [10, 11]

URT (ultrasound resonator technology) is considered to belong to the methods with an extremely high resolution in measurements of physical parameters of solutions and colloidal suspensions. The temperature behavior of various PNIPAM samples (block copolymers and microgels) has been studied.

Apparent activation free energies of the precipitation and re-dissolution of PNIPAM blocks have been determined for the first time. These are in the order of up to a few thousands kJ/mol, which can be explained by a high cooperativity of the precipitation process.

By combining TEM and AUC it was possible to show that PNIPAM at 40°C contains between 40 and 50 v-% of water. Besides free bulk water there is also bound water that strongly adheres to the N-isopropyl acrylamide units (about 25 v-%). Ultrasound resonator technology, which is non-sizing characterization method, revealed for PNIPAM microgel particles two more characteristic temperatures (at about 35 and between 40 and 50°C depending on the chemical nature) where distinctive changes in the ultrasound attenuation take place. Moreover, the experimental data suggests that the phase transition temperature is related to the surface charge density of the precipitated particles.

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Bio-Inspired Mineralization

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1991: Diploma, Physical Chemistry (University of Duisburg)
Thesis: Analytical Ultracentrifugation of Gels
1993: PhD, Physical Chemistry (University of Duisburg)
Thesis: Analytical Ultracentrifugation of Gels
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Since 1995: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
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This project investigates biomineralization **[1]**, practical aspects of biominerals like teeth **[2, 3]**, bio-inspired mineralization **[4-6]** as well as the underlying principles and crystallization pathways in an attempt to understand and apply Nature's toolbox for the synthesis of sophisticated and complex hierarchical materials **[7]**. Such processes can be very advantageously controlled by polymer additives **[8-10]**. Amorphous precursor phases, which can be moulded into any desired shape prior to crystallization, are often found along these crystallization pathways. This strategy is applied by Nature but can also be mimicked for the generation of single crystals with complex form **[6]**. In addition, amorphous phases are involved in the polymorph control of minerals as could be demonstrated for $CaCO_3$ **[11]** – the Biomineral which we investigate most. Complex fluidic phases **[12]** or polymeric templates **[13, 14]** are also used to direct the crystallization event. It is for example possible to create nanopores with defined sizes in single crystals by templating with polymer micelles resulting in mesoporous single crystals **[15]**.

Besides these regulation mechanisms for crystallization control, we are particularly interested in so-called non-classical crystallization pathways and mesocrystals **[16, 17]**. Nonclassical crystallization is a crystallization pathway which is based on nanoparticles involving their controlled superstructure formation in contrast to classical crystallization, which is based on the attachment of single atoms, molecules or ions.

The mutual orientation of the nanoparticles can even reach crystallographic order. Such crystals are called mesocrystals as abbreviation for mesoscopically structured crystals which show single crystal diffraction and light polarization properties but are composed of nanoparticles **[16, 17]**. To code the alignment of nanoparticles into mutual order, precise engineering of nanoparticle surfaces is necessary. However, little is so far understood about the formation mechanism of mesocrystals. We have therefore established a synthesis method for additive free high energy $CaCO_3$ crystal surfaces **[18]**, which are usually not exposed, but regularly found in mesocrystals. These crystal faces as well as regular $CaCO_3$ crystal faces were investigated using single molecule force spectroscopy with the AFM **[19]**.

This method allows to quantitatively detect adsorption/desorption forces of polymers on crystal surfaces and to learn about the nature of these interaction forces. Such results are an important prerequisite for the general understanding of polymer controlled crystallization. Indeed, significant differences were already detected for rather similar neutral $CaCO_3$ faces showing that our understanding of the precise nature of a crystal surface in a solvent is not yet mature **[19]**. We have therefore also looked at the effect of competitive solvent adsorption on crystal surfaces **[20]**.

However, also only little is so far known about the formation mechanisms of mesocrystals and their fate along the crystallization pathway. If the nanoparticles in a mesocrystal are not at least weakly stabilized by a (polymer) additive, the nanoparticles can fuse their crystal surfaces, which are already in crystallographic alignment forming a single crystal. This fusion of crystal surfaces releases surface energy and could be monitored by small angle neutron scattering as demonstrated for DL-alanine by SANS showing that mesocrystals can be intermediates in the formation process of a single crystal **[21]**.

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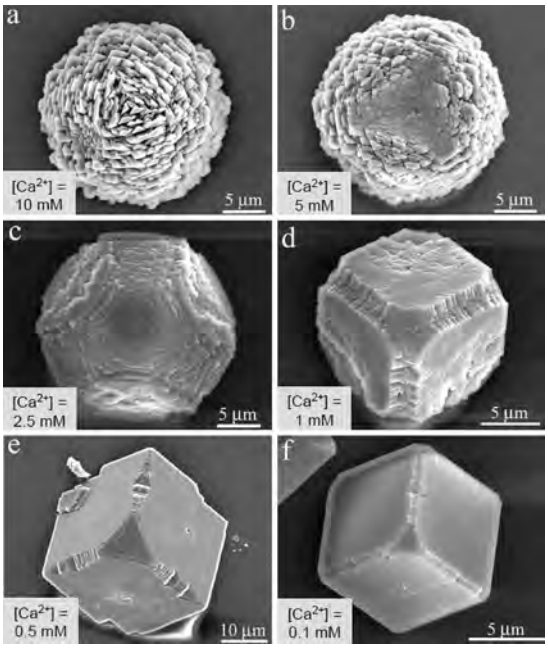

Fig. 1: Typical SEM images of calcite mesocrystals obtained different concentrations of Ca^{2+} and poly(ethyleneoxide)-block-poly(styrene-sulfonate) block copolymer with fixed [Ca] : [S] ratio of 1.25 : 1. Image taken from Ref. [22]

On the other hand, mesocrystals are the intermediate between a single crystal and a polycrystalline aggregate of nanoparticles without any mutual order, with a continuous transition between these two structures. This was demonstrated for $CaCO_3$, for which the structure could be tuned between a single crystal **(Fig. 1e)** and a polycrystalline aggregate **(Fig. 1a)** with increasing concentration of a structure directing block copolymer **[22] (see Fig. 1)**.

Single particle X-ray diffraction at the Bessy microfocus beamline revealed a single crystal diffraction pattern for the particle in **Fig. 1c** although this structure is composed of multiple nanoparticles. Even for the polycrystalline aggregate in **Fig. 1a**, which appears unordered, some preferential orientation was still detectable.

Mesocrystals can also be formed with hierarchical structure. This was demonstrated for $CaCO_3$ formed in the presence of a commercial copolymer poly(styrene-alt-maleic acid) **[23]**.

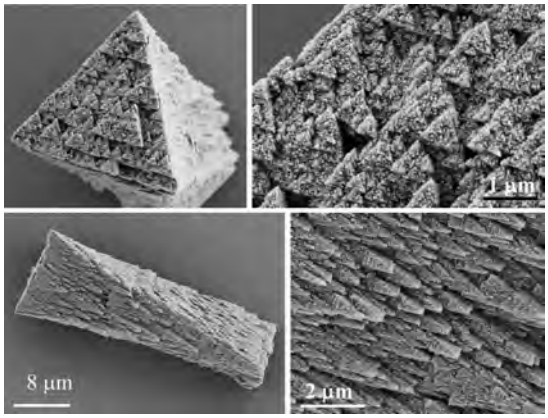

Fig. 2: SEM images of self-similar hierarchical calcite mesocrystals obtained at 1.25 mM [Ca^{2+}] and 0.1 g/l poly(styrene-alt-maleic acid) Image taken from Ref. [23]

The triangular end faces (**Fig. 2** upper images) are polymer stabilized charged {001} faces whereas the neutral {011} faces are also self similar (**Fig. 2** lower images) but are not covered by the polymer and are responsible for the orientation of the crystallites into crystallographic register **[23]**.

These results show that aggregation governs the length scales from a few tens of nm to a few tens of µm.

Investigations on the still smaller length scale down to the individual ions indicate, that even the primary nucleation event could be more an aggregation of stable $CaCO_3$ prenucleation clusters rather than an ion by ion growth as assumed in the classical theory of crystal growth **[24]**. The detected clusters form even in undersaturated $CaCO_3$ solutions where no nucleation occurs and are present already as soon as calcium and carbonate ions are mixed. These clusters were also found for the biominerals calcium oxalate and phosphate suggesting that clusters play a role in the precipitation of several minerals. Our results highlight the role of aggregation on different length scales in crystallization.

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Polymer-Bioconjugates as Macromolecular LEGO®-Bricks

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The combination of monomer-sequence defined peptides and common synthetic polymers proved to result in an interesting class of multifunctional block copolymers.**[1]** These bioconjugates are referred to as peptide-polymer conjugates.**[2]** Prospectively, they are of importance for biomedical applications e.g. for drug delivery and bio-host systems, but also to realize functional nanostructures or nanoelectronics.**[3-5]** Peptide-polymer conjugates exhibit significantly different properties compared to amphiphilic or double hydrophilic block copolymers.**[1]** Most evident differences result from the monodisperse character of the peptide segment. The defined amino acid sequence of a peptide allows encoding specific information into bioconjugates. Besides programming the self-assembly properties, biological activity can be integrated.**[6]** Moreover, responsiveness to external stimuli, catalytic activity, molecular recognition and defined interaction capabilities to inorganic, or organic surfaces can be realized with peptide-polymer conjugates **[7, 8]**. The integration of such specific properties into synthetic polymer systems certainly enlarges the structural and functional space available for polymer science.

Methodologies to Synthesize Bioconjugates

In order to selectively introduce peptides into synthetic polymers new synthesis routes had to be evaluated. These include coupling strategies (1) and polymerization strategies (2). Further developments of the coupling route include the utilization of the copper catalyzed Huisgen 3+2 dipolar cycloaddition. The "click" reaction of alkyne and azide functional species results in robust protocols to conjugate peptides and polymers.**[2]** Besides these advances, the polymerization strategy was developed further. Prior work applied atom transfer radical polymerization (ATRP) to graft synthetic polymers from peptides. Recently, the reversible addition-fragmentation chain transfer polymerization (RAFT) process was applied successfully. This proved to be a versatile synthesis platform to access well-defined peptide-polymer conjugates with adjustable molecular weights and low polydispersity indices (M_w/M_n ~1.1). The approaches for that rely on both dithioesters and trithiocarbonates as peptide based chain transfer agents (peptide-CTAs). Kinetic investigations reveal that both types control the polymerization of various monomers. Particularly the trithiocarbonates have been evidenced to be robust against nucleophiles, making it expectable that these CTAs will be exploited further to synthesize complex bioconjugates.

Bioinspired Formation of Structure and Function

Recent progress in exploiting peptides and proteins for material science applications improved structural control in polymer self-assembly. This has been identified as one key requirement to develop nanochemistry and nanotechnology strategies.

While the generation of specific functions in bioconjugates (i.e. programming self-assembly) has been in the focus of prior work, the regulation of such functions get mandatory. For instance, the peptide-guided organization process of bioconjugates could be developed further by introducing a switch concept, allowing to control rates of aggregation.**[9]** The introduction of temporary structure defects (switch-esters) into a peptide can suppress the self-assembly. However, the undisturbed peptide could be reestablished by a pH triggered O→N acyl transfer rearrangement. This provides a handle to regulate the aggregation kinetics of bioconjugates in water and organic solvents.**[10-12]**

With respect to the design of potent regulative mechanisms, posttranslational modification principles of proteins possess an enormous potential. Based on this, a strategy was established that utilizes enzymes to specifically modulate properties of peptide segments in peptide-polymer conjugates **(Fig. 1)**.**[21]**

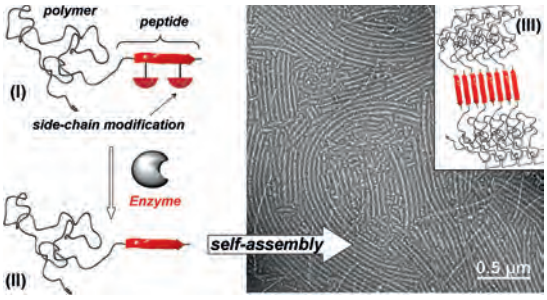

Fig. 1: Illustration of the BioSwitch process: Bioconjugate with suppressed aggregation tendency by O-phosphate modifications of threonine residues (I); enzymatic dephosphorylation activates the self-assembly tendency of the peptide (II), leading to fibrillar core-shell tapes (III, TEM micrograph stained with uranyl acetate).

To realize the *BioSwitch* process, a poly(ethylene oxide)-peptide (PEO-peptide) conjugate was synthesized that possesses a $(valine\text{-}threonine)_5$ aggregator domain. The introduction of phosphate moieties to the side chains of the threonine residues proved to disturb the peptide function and suppress the self-assembly process. Phosphatase could be applied to catalyze the hydrolysis of these phosphor monoesters. This restores the self-assembly tendency of the peptide segment and triggers the peptide-guided organization of the bioconjugate to form fibrillar structures **(Fig. 1)**. It can be expected, that the BioSwitch process seed further research exploring the highly specific tools of molecular biochemistry to enzymatically switch, transform, or crosslink peptides.

Besides developing means to regulate self-assembly processes of bioconjugates, the established concepts could be exploited to organize organic semiconductor segments.**[5]**

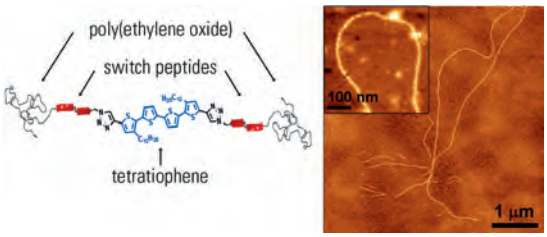

Fig. 2: Fibrillar "nanowires" formed by the directed self-assembly of a PEO-block-peptide-block-tetrathiophene-block-peptide-block-PEO ABA-conjugate (left). AFM micrograph of the fibrillar microstructures with the inset showing the left handed superhelical fine structure (right).

Functional microstructures could be obtained by combining a tetrathiophene segment with two PEO-peptide conjugates **(Fig. 2)**. The ABA-bioconjugate was synthesized via click ligation and a controlled self-assembly process was assured by using the switch concept. AFM investigations of the assembled structures revealed the formation of fibrillar nanoobjects with several micrometers in length and suggest the presence of a left-handed superhelical fine structure. The bioinspired organic semiconductor system represents an initial example of a novel class of biomimetic materials, rendering well-ordered optoelectronic segments by self-assembly of biological moieties, eventually generating advanced function by structuring of materials.

Mimicking Biomaterials

Biological inorganic-organic materials e.g. from glass sponges are high performance, fiber directed composites. For instance, the glass sponge *Euplectella sp.*, one of the most primitive animals in existence, realizes integrated composite materials based on glass. This biological silica morphogenesis process could be mimicked by providing self-assembled peptide-polymer nanotapes as structural scaffolds to guide the condensation of silicic acid. As a result of an integrated self-assembly-silification process, nanofiber-directed composite fibers formed spontaneously within seconds **(Fig. 3b)**. Detailed analysis of the material reveals six distinguishable levels of hierarchical order and excellent mechanical properties. **[7]** The rapid process, which leads to structured composites could be exploited to generate on the one hand distinct silica nanocomposite tapes under kinetic conditions **(Fig. 3a)**. **[14]** On the other hand a convenient 2D-plotting process could be established that enables one to draw macroscopic networks of nanostructured silica composite fibers **(Fig. 3c)**. **[15]**

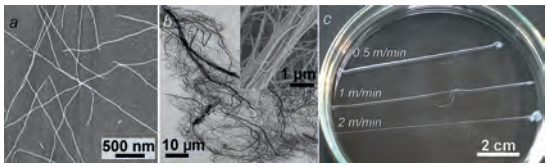

Fig. 3: Biomimetic silica composite fibers (AFM image of silica composite nanotapes (a), light microscopy and SEM micrographs of the macroscopic silica composite fibers (b & b, inset) and plotted biomimetic silica composites (c)).

Biological and Biomedical Applications

The development of defined peptide-polymer conjugates allows addressing pharmacological and biomedical issues. **[4, 6, 16]** On the one hand peptide-poly(*N*-isopropyl acrylamide) conjugates could be utilized to modify gold substrates. **[6]** This realizes surfaces with specific bioactivity, where the biological property could be reversible switched from cell attractant to cell repellent, depending on temperature.

On the other hand biocompatible carriers for drug delivery have been developed, e.g. to transport DNA for gene delivery applications. For that, a synthesis route to PEO-poly(amido amine) conjugates (PEO-PAA) was explored. **[16]** The strategy enables the synthesis of PEO-PAA conjugates with monodisperse PAA segments. Thus, the cationic character (balance and sequence of tert., sec., and prim. amine groups) can be programmed, making the fine tuning of the interaction capabilities of the carrier with plasmid DNA (*ds*DNA) feasible. **[3, 17]** PEO-PAAs are well-defined model compounds, that exhibit low toxicity and sharp property profiles. This makes the class of precision polymers ideal to correlate e.g. the cationic balance of the PAA segments with the DNA complexation and compression properties as well as with membrane translocation and transfection activities.

Outlook

Bioconjugates and particularly peptide-polymer conjugates have been developed in the recent years to a multifunctional platform of precision polymers. The monodisperse character of the functional (pseudo)peptide segments allows for the precise definition of macromolecules and macromolecular properties. Thus, molecular toolboxes are provided to precisely define interaction capabilities, structure formation, and biological activity of interfaces. Moreover, the generation of distinct functions by positioning of functionalities can be achieved, which might drive research in various fields from nano-technology to biomedicine.

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Bioinspired Polymers and Colloids

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Polymers: Synthesis

The radical addition of thiols onto 1,2-polybutadiene is a versatile route for the generation of a toolbox of functional polymers **[4, 10, 17, 19]**. Thiyl radicals can be produced via a radical source at elevated temperature or directly through irradiation with UV light or sunlight **[16]**. The degree of functionalization is usually less than quantitative, which is due to a side reaction of the intermediate radical species leading to the formation of six-member cycles along the polymer backbone. Such side reaction can be avoided when 1,2-polybutadiene is replaced by poly[2-(3-butenyl)-2-oxazoline] **(Fig. 1)**. The modification of the poly(oxazoline) with thiol has the characteristics of a "click" reaction, enabling the synthesis of highly hydrophobic fluoropolymers in the same way as that of water-soluble glycopolymers **[7, 11, 18]**.

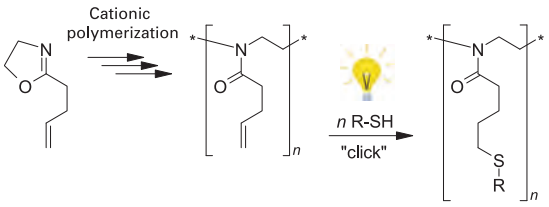

Fig. 1: Synthesis and click modification of poly[2-(3-butenyl)-2-oxazoline].

Colloids: Polyoxazolines

Annealing of an dilute aqueous solution of poly(2-isopropyl-2-oxazoline) above its cloud point leads to the formation of coagulate in the form of crystalline nanofibers **(Fig. 2)** with a melting point of about 195°C. Directional crystallization, which occurs below the glass transition of the polymer at 65°C, is driven by hydrophobic and dipolar interactions in combination with a solvation effect **[3, 8]**.

Glycosylated polyoxazoline homopolymers, consisting of a hydrophilic tertiary polyamide backbone and hydrophilic D-glucose side chains, can self-assemble into spherical vesicles and nanofibers upon direct dissolution in water. Based on transmission electron and scanning force microscopy and small-angle X-ray scattering data, it is proposed that nanofibers are hollow nanotubes with a cross-sectional radius of less than 10 nm and a wall having a thickness of about 1 nm. As evidenced by spectroscopy, the wall should be constructed of chains forming a sheet through intermolecular hydrogen bonding between amide and glucose units **(Fig. 3) [11, 18]**.

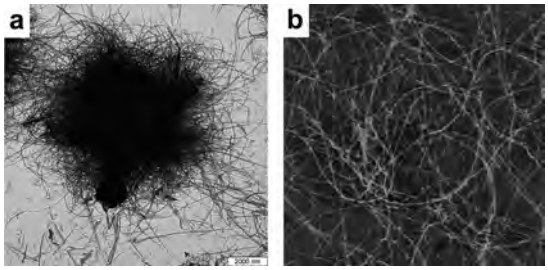

Fig. 2: (a) Transmission electron image of coagulate particles produced by poly(2-isopropyl-2-oxazoline) in pure water (scale bar = 2 µm). b) SFM topography image (10 x 10 µm^2) of the coagulate formed under stirring in a mixture of water and tetrahydrofuran 98:2 (v/v) within 24 h at 65°C.

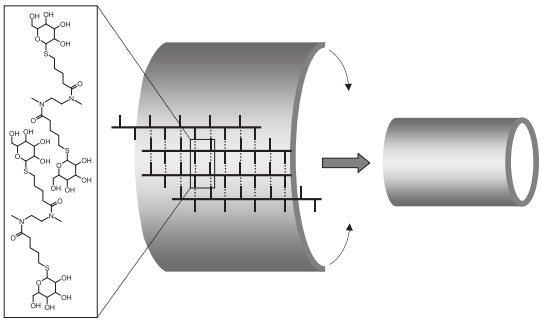

Fig. 3: Tentative idealized structure of the hydrogen-bonded glycosylated polyoxazoline layer (hydrogen bonds are indicated as dotted lines) and subsequent bending and closing into a nanotube.

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Colloids: Polypeptides

Combined dynamic and static light scattering was applied to study the vesicles of polybutadiene$_{165}$-*block*-poly(L-lysine)$_{88}$ in dilute saline solution at pH 7.0 (polypeptide in 100 % coil conformation) and pH 10.3 (polypeptide in 80 % α-helical conformation). At the higher pH, the vesicles were considerably smaller in size (hydrodynamic radius: 364 nm → 215 nm) and chains were more densely packed at the core-corona interface (inter-chain distance, b: 3.2 nm → 2.4 nm) **(Fig. 4)**. Changes in size and structure can be explained in basic terms of colloid stabilization without considering any secondary structure effect **[5]**.

Structure formation in solutions of a polystyrene$_{63}$-*block*-{poly(γ-benzyl-L-glutamate)$_{37}$}$_8$ hetero-arm star block copolymer, obtained by swelling thin films in chloroform solvent vapor, were investigated by optical and scanning force microscopy (SFM). Direct observation by optical microscopy revealed the nucleation and growth of ordered three-dimensional structures of ellipsoidal shape **(Fig. 5)**. The process of structure formation is considerably affected by the presence of water. The observed effect is attributed to changes in the solubility of the polymer in chloroform due to a complexation of water molecules with the α-helical polypeptide chains **[12]**.

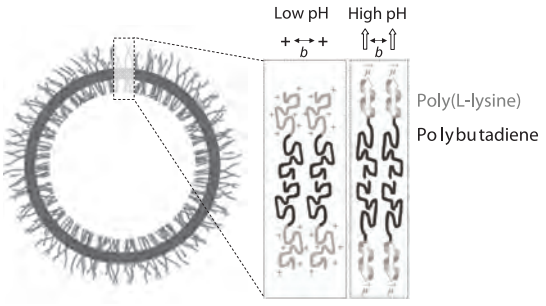

Fig. 4: Tentative structures of PB_{165}-b-$PLLys_{88}$ vesicles at different pH.

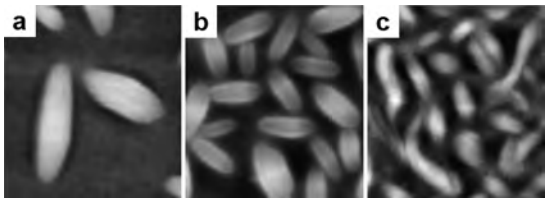

Fig. 5: SFM topography images (2.5 x 2.5 µm^2) of the ellipsoidal structures formed in solutions of polystyrene$_{63}$-block-{poly(γ-benzyl-L-glutamate)$_{37}$}$_8$ in chloroform at different concentrations: a) 53 %, b) 55 %, c) 57 %.

H. Schlaad, J. Brandt, M. Gräwert, A.L. Demirel, A. Bertin, Z. Hordyjewicz-Baran, L. You, A. Gress, F. Hermes, C. Diehl, N. ten Brummelhuis,
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Fractionating Colloid Analytics

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Analytical Ultracentrifugation (AUC) is a powerful fractionating analysis method 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 is used in multiple studies which are not cited here. We follow three main working directions in this project: a) detector development, b) method development c) colloid and polymer characterization. For the latter it was laid special emphasis on complex polymer and colloid systems, which can not be characterized by other analytical methods with the same information content.

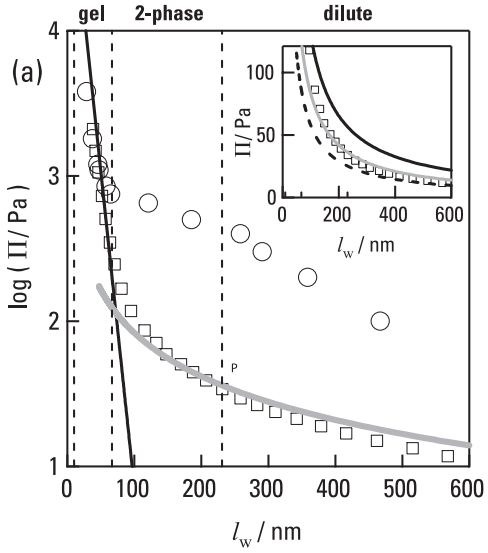

Fig. 1: Osmotic pressure (log scale) plotted against water layer thickness, l_w for disc-like laponite RD particles of thickness 1 nm and diameter 25 nm. Open squares: AUC experimental data; open circles: literature experimental data from osmotic stress experiments. Solid line in the high and low concentration regime: theoretical osmotic pressure. Vertical lines delineate the literature-determined phase boundaries at l_w = 67 and 230 nm, and the Debye length for 10^{-3} M salt, of ~10 nm. Inset: The experimental data in the low-concentration regime, and the calculated osmotic pressure for average particle diameters of 20 nm (solid black line), 25 nm (grey line) and 30 nm (dashed black line), shown on a linear scale.[1]

We have developed the methodology to characterize the osmotic pressure of solutions or swelling pressure of gels by AUC further, to include the determination of the equation of state of liquid crystalline systems via osmotic pressure measurements in sedimentation equilibrium. **[1]** These measurements include the determination of phase boundaries, which are very difficult to obtain otherwise. For laponite clay dispersions, it could be demonstrated that a continuous dependence of the osmotic pressure, over orders of magnitude between at least ~10^1 and 10^4Pa, and a wide concentration range, can be determined in agreement with standard theoretical considerations in one experiment. Two regimes – counter-ion ideal gas and interacting double layers – can be easily identified in the equation of state, whereas meta-stable glass- or microphase-separated gel states previously encountered in osmotic stress measurements of laponite are circumvented. **[1] Fig. 1** shows the good agreement of the measured osmotic pressures with those derived from theoretical models for the dilute and concentrated regime. These results show the advantage of the AUC experiment, which yields hundreds of osmotic pressure concentration pairs over the traditional time consuming osmotic stress approach which yields only a single data pair. Also the possibility to investigate multiphase systems and phase boundaries in a single experiment demonstrates the power of the approach.

The ultracentrifuge can also be applied to separate samples according to their density by the established technique of density gradient ultracentrifugation. Although density gradient techniques have been well-established for decades to separate various biopolymers from mixtures or biopolymers with subtle density differences like single- and double-stranded DNA, the methodology can still be developed – in our case for the separation of racemates from pure enantiomers **(Fig. 2)**.

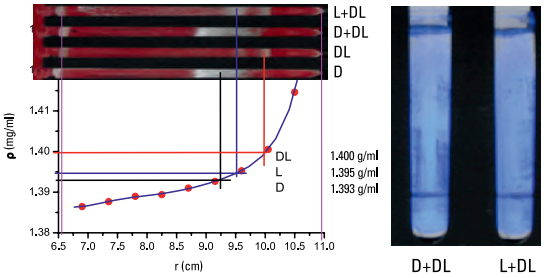

Fig. 2: Separation of DL-alanin crystals from the pure enantiomer crystals by density gradient ultracentrifugation in a Nycodenz gradient. The left figure (upper) shows the bands in the ultracentrifuge tubes and the lower part shows the corresponding calibration curve which allows the determination of the sample density. The right figure shows the separation of L- resp. D-alanin (upper band at meniscus) from the denser racemate (lower band) with a Nycodenz solution with intermediate density [2].

This separation is based on the fact that solid racemic compounds differ significantly in density from the corresponding pure enantiomers. This difference can be as large as 5 %. The racemic compounds in the solid state are denser than the corresponding enantiomers so that pure enantiomers can be separated from racemates even on a preparative scale by density gradient ultracentrifugation. **[2] Fig. 2** shows that the bands for the different compounds can be clearly separated although the density difference between them is very small and in the third decimal digit. This shows that the density accuracy is high and in the third digit in density while also good recovery rates between 75 and 90 % are achieved. **[2]** This procedure is a simple method for the separation of enantiomers from racemates, which so far is only possible by expensive methods.

The third focus of our work was the further development of the multiwavelength detector for the AUC. **[3]** We have carried out systematic performance tests and found that our detector prototype yields data of a similar or better quality than the commercial Beckman XL-A instrument, although a whole range of wavelengths is acquired instead of a single wavelength as in the commercial instrument (for an experimental scan see **Fig. 3**). The multiwavelength detector is now in a stage to become applicable for routine operation.

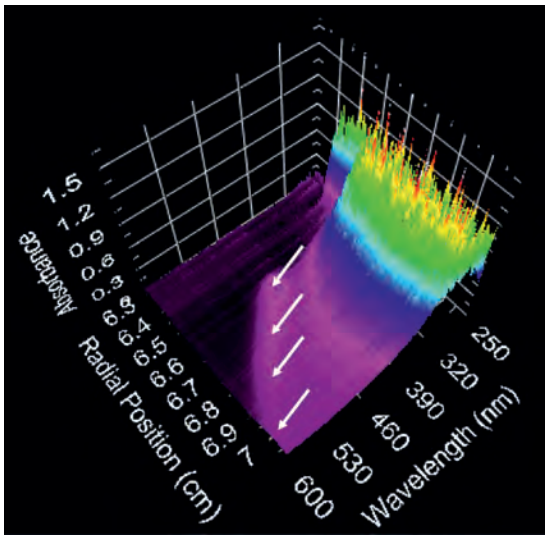

Fig. 3: Raw scan from the multiwavelength detector for the AUC on a CdTe nanoparticle sample. The blue shift of the absorption maximum (white arrows) with decreasing particle size at decreasing radial distance is visible. Sedimentation proceeds towards higher radii.

First experiments demonstrate the virtue of this detector, which is able to continuously measure size dependent optical properties of colloids. One example is shown in **Fig. 3** where CdTe quantum size nanoparticles were separated in the AUC according to the particle size (proportional to the radial position in the shown raw data). Already in the raw data, the blue shift of the absorption maximum (white arrows) with decreasing size (radial position) is obvious. This enables a few hundred correlations of size dependent optical properties in a single sedimentation velocity experiment lasting a few hours. It has to be emphasized that **Fig. 3** just shows unprocessed raw data from a single time scan in the multiwavelength AUC. This indicates the gain in information content from AUC data, which can be achieved with this detector. We will now start to use this detector technology for the determination of size dependent optical properties of various colloids and start its use for routine operation in the AUC service unit in the institute.

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Electron Microscopic Studies of Colloidal Systems and Biomaterials

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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, fibers, aggregates of biopolymers, polyelectrolyte complex shells, composite materials and naturally-grown biomaterials. Because of the organization of the institute, there is a close coope-ration with a number of research groups of the colloid chemistry, interface and biomaterials departments and the University of Potsdam. On the other hand, the electron microscopy lab is a so called central service lab to perform scientific routine measurements for the whole institute. Selected interesting results are presented here.

Basically polymers exhibit critical solution behavior dependent on temperature, simply because of the thermodynamics of polymer-solvent interactions.

A critical solution behavior could be observed for quite a number of polymers. Especially in biomedical applications the temperature at which a polymer becomes insoluble should be close to human body temperature and relatively insensitive to changes in environmental conditions. The lower critical solution temperature of poly(2-isopropyl-2-oxazoline) (PIPOX) can be triggered in a wide temperature range (~30-80°C) by changing concentration and molecular weight as well as by adding salts and surfactants.

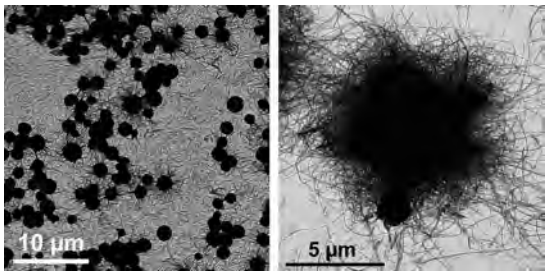

Fig. 1: Dried coagulate particles formed by $PIPOX_{47}^{+}$ in water through annealing for 24 h at 65 °C.

Annealing of dilute aqueous solutions of PIPOX at above the cloud point leads to the irreversible formation of coagulate particles with hierarchical ordering on two length-scales. **Fig. 1** shows exemplarily transmission electron micrographs of the dried coagulate produced by $PIPOX_{47}^{+}$ in water at pH ~6.5. The concentration of polymer was 0.05 % by weight. One can see two types of structures on two different levels of length-scale, namely micron-sized spherical particles together with fibrils having a cross-sectional diameter of about 30-50 nm and a length of several microns. The microspheres are amazingly uniform in size and shape. They are densely packed and actually built of these fibrillar aggregates. Neither the inner structure of PIPOX fibrils nor the mechanism of self-assembly of fibrils into spheres is known yet. Further investigations by solid-state NMR and electron diffraction experiments as well as by time-resolved imaging shall be performed to gain a better understanding of this self-organization process.

Another interesting subject is the synthesis of functional silica-based materials, enabling one to conveniently draw nanostructured, macroscopic networks of oriented silica composite fibers, which can be used as precursors for fabrics of mesoporous silica fibers. Studies addressed the control of hierarchical nano- and microstructures, porosity, chirality as well as surface functionality. By using self-assembled PEO-peptide nanotapes as an ink to draw the composite fibers, the macroscopic form of the fiber networks, the line width, and both network orientation as well as network anisotropy can be defined. The local injection of PEO-peptide nanotapes into a thin layer of a dilute solution of pre-hydrolyzed TMOS leads to a rapid formation of the composite fibers, which exhibit several levels of hierarchical order. The rate of plotting is a parameter, enabling one to control the line width and the orientation of the nano- and sub-micrometer structure elements in the network.

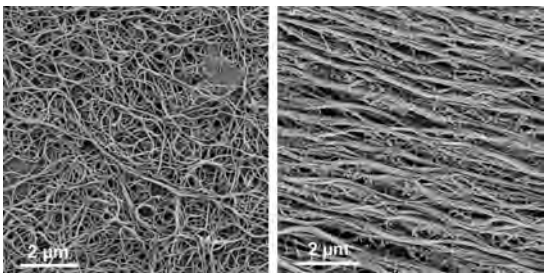

Fig. 2: Silica composite fiber morphology, plotted with different rates of 0.5 m . min^{-1} (left) and 2 m . min^{-1} (right).

Fig. 2 shows the morphological structure of silica composite fibers, plotted with a constant rate of nanotape injection (0.2 mL . min^{-1}, 4 mg nanotapes per min) at different plotting rates. Interestingly, rather flat, fiber structures are generated. Due to the cooperative nature of the composite fiber formation, both the silicification and the self-assembly processes strongly depend on the rate of silicic acid influx to the places of composite fiber formation. However, the well-defined width and sharp boundaries of the composite macrofibers suggest that indeed a critical cross-link density is reached rapidly, preventing axial diffusion of the nanotapes (e.g. **Fig. 2** left). The SEM micrographs show a homogeneous network, composed of rather uniform fiber elements with diameter of about 60 to 100 nm. Moreover, the same complex structure and corresponding levels of hierarchical order are evident, suggesting that the formation of the plotted and batch composite fibers occurs via analogous silicification self-assembly processes.

Acoustic waves with higher frequencies interacting with a species can cause structural changes and accelerate chemical reactions. The majority of sonochemical reactions in aqueous solutions applying acoustic vibrations is caused by cavitation. To examine the influence of ultrasonic treatment on the activity and crystalline structure, Pt nanoparticles were sonicated e.g. in water.

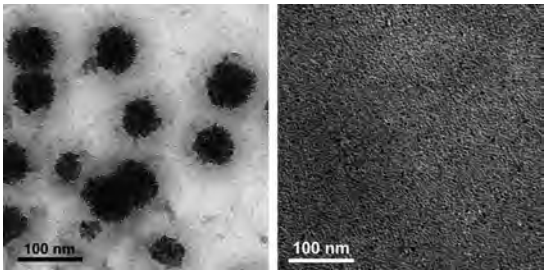

Fig. 3: TEM micrographs of platinum nanoparticles before (left) and after 60 min sonication in water (right).

They were stabilized with citrate ions, resulting in assemblies of spherical shape **(Fig. 3 left)**. The size of preformed Pt nanoparticles assemblies is varying from 50 nm to 80 nm in diameter. After 1 h of ultrasonic treatment a complete decomposition of these Pt assemblies was observed and only small Pt nanoparticles in the range of 3 nm to 6 nm were obtained **(Fig. 3 right)**. In this case very interesting opposite effects on the crystalline structure, depending on sonication time, were found for Pt nanoparticles.

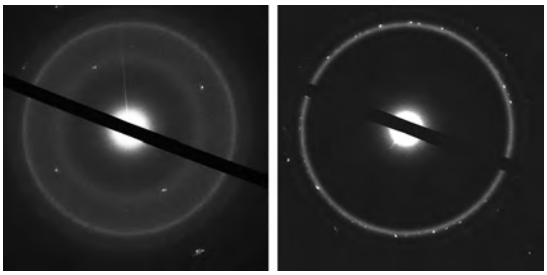

Fig. 4: Electron diffraction pattern of platinum nanoparticles before (left) and after 60 min sonication in water (right).

Both thin sharp and diffuse rings with several spots were observed in the diffraction pattern of the Pt nanoparticles before sonication **(Fig. 4 left)**. Diffuse rings are due to small platinum grains, whereas the sharp ones are mainly ascribed to their assemblies. The presence of bright sharp dots points to the specific orientation of small platinum seeds. Narrow diffraction rings were turn found for Pt nanoparticles after ultrasonic treatment for 1 h **(Fig. 4 right)**. The change from diffuse to sharp rings is characteristic of recrystallization of the platinum nanoparticles.

Another important project is the electron microscopic characterization of highly ordered arrays of metallic Au nanostructures. Monodisperse polymer spheres of submicrons to microns in size can readily self-assemble into ordered and closepacked arrays on the surfaces of the substrate. Using angle-resolved colloidal lithography and O_2-plasma etched bilayers of hexagonally packed spheres as templates, well ordered arrays of gold nanoparticles with different shapes are formed. The size and shape of Au nanoparticles obtained can be manipulated by the plasma etching period and the incidence angle of Au vapor flow. The subsequent thermal annealing at 900 °C for 60 min in ambient led to hexagonally arranged arrays of small and big Au nanoparticles with a nearly round shape **(Fig. 5)**. Prior to Au vapor deposition, the bilayers of hexagonally close-packed 830 nm PS spheres were etched by O_2-plasma for different time periods. Subsequently, they were used as masks for Au vapor deposition at the incidence angle of 15°. After decomposition of the PS bilayer masks with toluene, the resulting Au nanostructures are investigated by scanning electron microscopy.

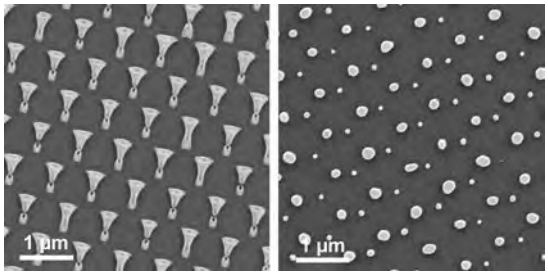

Fig. 5: Hexagonally arranged Au nanoshuttlecocks obtained by using bilayers of hexagonal close-packed PS spheres, etched by O_2-plasma for 25 min (left). Hexagonal binary arrays obtained by annealing the nanoshuttlecock arrays (right).

The periodicity remained little varied, about 830 nm. This approach should pave a versatile colloidal way to form binary nanoparticle arrays for technical applications such as nanoelectronics and nanophotonics.

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From Hard to Soft Porous Frameworks

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Nanostructured materials have been subject of recent study because of their unusual mechanical, electrical and optical properties which arise from confinement effects and the combined properties of bulk and surface. One challenge crucial for applications like catalysis, sensing or separation is the control of the functionality, nano- and macrostructure of these materials. Our group is investigating materials that combine these features with the main focus on the preparation of materials with pores of nano-sized dimensions. Several materials are under investigation ranging from "hard" inorganic materials to "soft" organic materials.

Carbon Nitrides

Graphitic carbon nitrides (g-C_3N_4) can be prepared by thermal condensation of simple precursors like dicyandiamide or melamine **[1]**. Following a reaction/condensation scheme the resulting materials adopt a structure characterized by graphitic stacking of layers composed of interlinked heptazine units. New synthetic conditions for carbon nitride materials are explored, e.g. temperature induced condensation of dicyandiamide in salt melts as a solvent, yielded highly crystalline, graphitic carbon nitride, which is expressed in the formation of macroscopic crystals in the form of hexagonal prisms **[2]**.

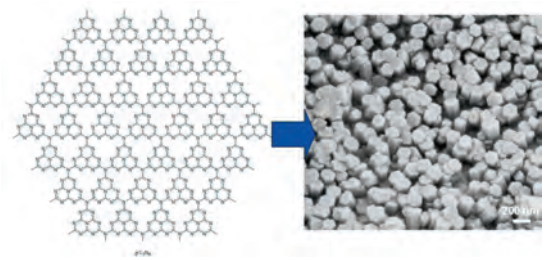

Fig. 1: The schematic internal structure of g-C_3N_4 is reflected in the crystal morphology. SEM images of crystalline graphitic carbon nitride prepared in molten salt show hexagonal prisms.

Metal Nitrides

Metal nitrides have considerable prospects as catalysts or optoelectronic materials, however in contrast to their corresponding metal oxides, a general synthetic strategy for the control of their nanostructure, porosity and surface area was not envisaged yet. Using an approach called "Reactive Templating", metal nitrides with variable nanostructure and composition can be prepared **[3-5]**. In this approach nanostructured carbon nitrides are used as both, a template and a nitrogen source yielding the metal nitride. The so-prepared metal nitrides exhibit high surface areas and a remarkable activity as catalytic materials **[6]**.

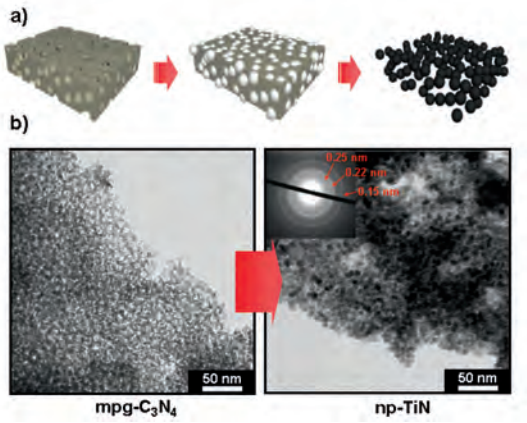

Fig. 2 a) Scheme of the "reactive templating" approach for the synthesis of metal nitride nanoparticles from mesoporous graphitic carbon nitrides b) TEM micrograph of mpg-C_3N_4 and titanium nitride nanoparticles generated there from.

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Self-Assembled Microporous Polymers

Polymers with highly rigid and contorted molecular structures prevent space-efficient packing in the solid-state and can consequently exhibit microporosity. Recently, we were able to apply this concept to common polymers like aromatic poly(imide)s or poly(amide)s **[7]**. A desirable motif that prevents space-efficient packing or crystallization is a 90° kink within the polymer chain, for example provided by difunctionalized spirobifluorens. Soluble aromatic polyimides exhibiting high surface areas in their solid state have been synthesized using this structure directing motif.

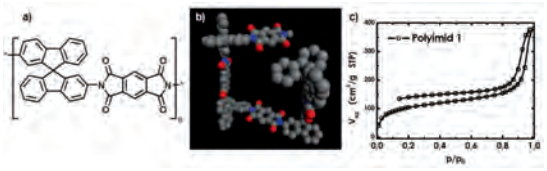

Fig. 3: a) Chemical structure of a microporous polyimide generated by incorporation of spirounits into the polymer chain. b) Calculated conformation of Polyimide 1 c) Nitrogen sorption isotherm for PI-1

A similar concept was used for the formation of microporous cross-linked polymer networks yielding polymers with surface areas of more then 1000 m^2/g **[8]**. Also networks composed of conjugated polymers, for example based on polyparaphenylenes or polythiophenes have been produced **[9-10]**.

Organic Frameworks

Combining classical elements of the synthesis of inorganic materials and (organic) polymerizations, the synthesis of highly porous, covalent organic frameworks have been achieved by carrying out trimerization reactions of dicyanocompounds in molten zinc chloride **[11]**. Using the suitable reaction conditions, which enable a dynamic, reversible trimerization reaction of the carbonitriles, triazine-based covalent organic frameworks with high surface areas could be produced. Further heat treatment even produced materials with surface areas of more than 3000 m^2/g **[12-14]**.

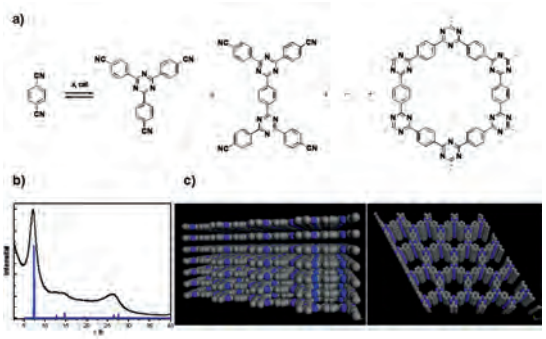

Fig. 4: a) Schematic presentation of the trimerization reaction of dicyanobenzene into a covalent triazine-based framework (CTF-1). b) Experimental (black) and calculated (blue) WAXS diffractogramm of a triazine network made from 1,4-dicyanobenzene. c) Schematic representation of the structure of CTF-1.

Compared to other widely used catalyst-support materials, such as activated carbons these frameworks provide a high amount of selective binding sites for metals and thus have extraordinary prospects as catalyst support material as well as for hydrogen or methane storage materials.

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Sustainable Functional Nanostructured Materials

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The concept of Sustainable Chemistry represents an area of innovation, which not only preserves resources but also stands for a development process in the chemical industry. Sustainable Chemistry aspires to raise the stake of less dangerous chemicals as well as production of environmentally high-quality products from preferable renewable resources.

Our research is focused on the production of nanostructured materials of practical importance- starting from low cost natural precursors and using environmentally friendly processes. It is known that a material, regardless if organic or inorganic, improves its properties when scaled down to the nanometer region. Therefore mesoporous nanostructured materials such as polymers, carbons or metal oxides produced via a green chemistry route can offer attractive fields of applications e.g. in catalysis, chromatography, adsorption, sensors, energy storage and electrochemical processes.

Hydrothermal Carbon

a) Nanostructured Carbon Materials

The synthesis of carbonaceous materials generally relies on very harsh conditions e.g. electric-arc discharge techniques, catalytical chemical vapour deposition, catalytic pyrolysis of organic compounds or high-temperature hydrothermal conversion at 800 °C from amorphous carbon.

Therefore, the search for new strategies to generate carbon materials, carbon hybrids and related materials has been of major importance in material chemistry. Hydrothermal carbonization, involving the hydrothermal decomposition of various carbohydrates in aqueous solutions at 180°C represents one of these strategies towards a green and cheap method to directly produce spherically shaped functional carbon from carbohydrates **(Fig. 1)** **[1, 2, 3]**. A major advantage of this method is that due to the mild temperature conditions, the as synthesized particles contain functional groups confined to the surface and thus are hydrophilic. Therefore further activation processes are not necessary. Additionally, this enables us to further functionalize the particles in order to fit various applications.

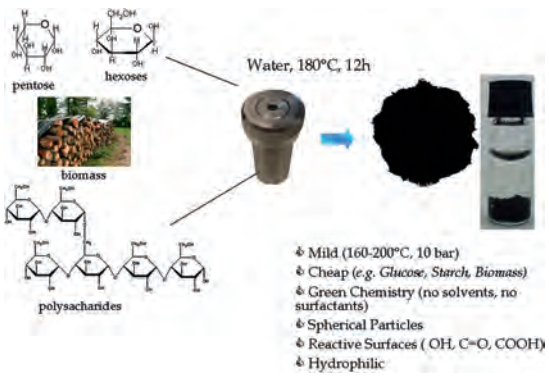

Fig.1: Hydrothermal carbonization process

The porosity of hydrothermal carbon can be controlled by introducing suitable templates into the synthesis **[4, 5]**. Thus, performing the hydrothermal carbonization in the presence of various nanostructured silica materials followed by their removal we can produce mesoporous functional hydrophilic carbons materials. Such a low temperature route towards porous carbon materials with controllable surface functional groups and reactivity has a great potential for a variety of applications such as catalysis, chromatography, adsorption and Li insertion.

Another very interesting aspect of the hydrothermal carbonization process is that instead of pure carbohydrates, low value biomass residues can be used as a carbon precursor **[6, 7]**. This represents a meaningful way to transfer biomass into useful materials, more efficient energy carriers and/or carbon storage deposits therefore an efficient process to remove atmospheric CO_2 by fast growing plants, finally forming a carbon sequestering solid.

b) Carbon Nanocomposites

Using hydrothermal carbonization in the presence of water soluble metal salts or preformed nanoparticles, we can obtain carbon/metal (oxide) nanocomposites in a one step process **[8]**. These nanocomposites have important applications in the field of catalysis and electrochemistry. For example the hydrophilic C/Pd carbon nanocomposites were successfully used for the selective hydrogenation of phenol to cyclohexanone in aqueous phase **[9]**. Furthermore, the carbon matrix can be removed from these nanocomposites by simple calcination.

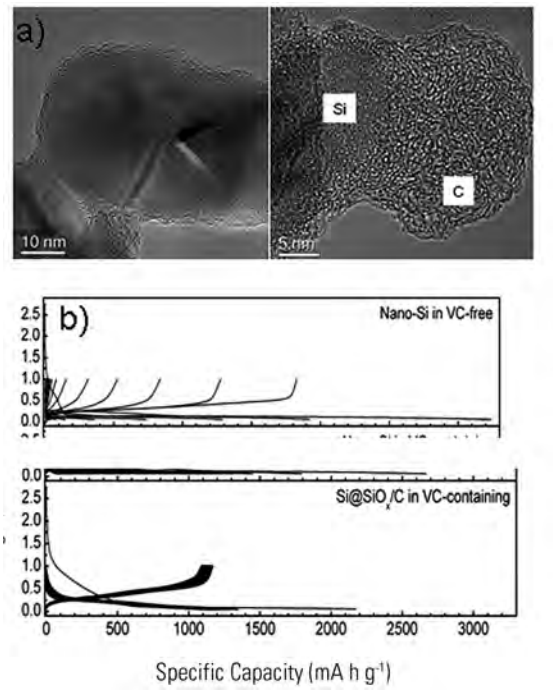

Fig.2: a) Silicon/carbon naocomposites showing core/shell morphology; b) Electrochemical performance of pure silicon nanomaprticles (up image) in comparison with the carbon coated nanoparticles (down image) showing an improved cycling performance (60 cycles)

When coating silicon nanoparticles with hydrothermal carbon, a nanocomposite showing a significant improved lithium storage performance in terms of a highly reversible lithium storage capacity, excellent cycling performance and high rate capability has been obtained. This represents a promising candidate as an anode material in lithium-ion batteries **(Fig. 2) [10, 11, 12]**.

Additionally, water soluble, functional organic monomers can also be introduced into this process resulting in carbonaceous materials with increased functionality with applications in water treatment or catalysis **[13, 14]**

c) Nitrogen-Doped Carbon

Recently, nitrogen-containing carbons are the subject of particular interest to researchers due to their remarkable performance in applications such as CO_2 sequestration, removals of contaminants from gas and liquid phases, environmental protection industry, catalysts and catalysts supports, or in electrochemistry as supercapacitors, cells and batteries to improve their capacity parameters.

Here, we present green and sustainable alternatives to produce nitrogen rich carbons which are based on the hydrothermal carbonization of nitrogen containing carbohydrates such as chitosane or glucosamine or on hydrothermal carbonization of glucose in the presence of different proteins **(Fig. 3) [15, 16]**. The resulting materials are carbon like material containing up to 9% nitrogen while the level of structural order can be improved by further carbonization at higher temperatures maintaining the nitrogen content constant. Given the simplicity of this method and the low cost of the starting precursors we believe that this method represents a sustainable alternative for the production of nitrogen containing materials.

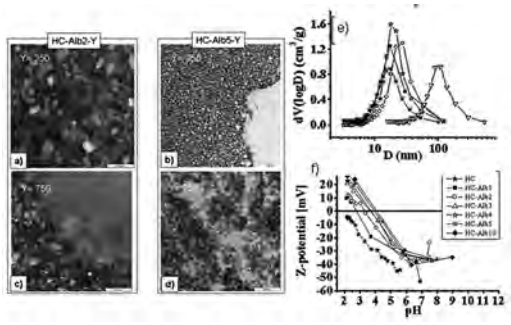

Fig.3: a) TEM micrograph of nitrogen doped carbon obtained from hydrothermal carbonization of glucose in the presence of a, b) 2% albumine; c, d) 5% albumine e) pore size distribution of the nitrogen doped materials showing their nanostructured character f) zeta potential measurements proving the positive charge of the materials at negatives pH due to nitrogen protonation

Smart Polymers

a) Thermoresponsive Polymers

Stimuli-responsible polymers can change their structural and physico-chemical properties in response to external signals. Among the thermo responsive polymers, poly-N-isopropylacrylamide (PNIPAAm) has the sharpest phase transition in the class of N-alkylacrylamide polymers. PNIPAAm exhibits thermally reversible soluble-insoluble changes in aqueous solution as a response to temperature across a lower critical solution temperature (LCST) at 32°C. Due to this temperature dependent behaviour PNIPAAm grafted surfaces exhibit temperature-responsive hydrophilic-hydrophobic surface property alterations. Our research is focused in grafting of PNIPAAm and other thermoresponsive polymers, alone or in combination with other co-monomers, onto pre-synthesised silica or polymeric monoliths using controlled polymerization techniques **[17]**. The resulting monolithic hybrid material is used as a separation platform in chromatography for the separation of bioactive macromolecules in a pure aqueous environment and under isocratic conditions by simply changing the temperature of the chromatographic column **[18]**. **Fig. 4** illustrates this concept for the separation of a mixture of steroids based on hydrophobic interactions.

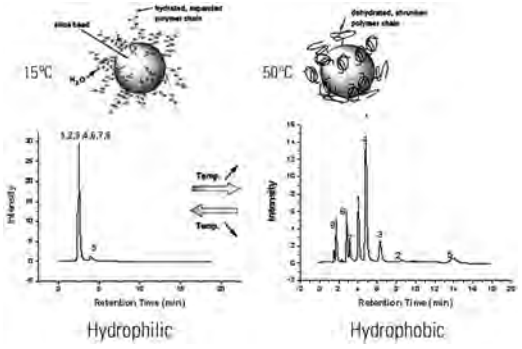

Fig.4: Temperature responsive chromatography of a mixture of steroids

b) Molecularly Imprinted Polymers

The assembly of a recognition site around a template molecule can be achieved within highly cross-linked polymeric matrices using molecularly imprinted techniques where the complementary functionality is introduced in the form of polymerisable monomers. We are interested in synthesizing molecular imprinted monoliths capable of recognizing and separating larger biomolecules such as peptides and proteins **[19, 20]**. Our procedure consists in immobilizing our target molecule or a small epitope of it onto the surface of a hierarchical porous silica monolith. After immobilization, the pore structure of the monolith is filled with a mixture of functional monomer and cross-linker. The functional monomer will interact with the pore-wall immobilized template, and following the removal of the silica monolith a polymeric monolithic materials will be obtain that will have the binding sites confined to the surface. This will allow substructures of larger molecules to be recognized by the surface-exposed sites. Furthermore, this process can be combined with the introduction of a thermoresponsive monomer resulting thus in stimuli responsive imprinted polymeric monolithic materials with great potential for separation science.

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De Novo Nanoparticles: Novel Synthetic Routes for Nanoparticle Production

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1. Introduction

Nanoparticles are an astonishing type of matter. Simply by finely dispersing common bulk materials new properties can be observed **[1]**. This is mainly due to the fact that atoms at surfaces behave differently to those in the bulk, and nanoparticles are literally characterised by those surfaces. But there is more: when properly assembled or combined with well-known materials, the resulting nanostructures can shown unexpected performances so that, for instance, inert materials can turn reactive, conductor when insulator, or simply harder, lighter, more robust, etc. The futuristic speech of Richard Feynman "*There's plenty of room at the bottom*" (1959) **[2]** from which the nanotechnology age had start, it is a concrete concept today and saying that nanotechnology will change human life, it is not too hazardous.

However, if unforeseeable behavior of materials at the nanoscale represent the charm of "nano-science", on the other hand it makes difficult to understand why such behaviour show up or can be tuned. For this reason, for many applications, appropriate nanostructures do not already exist or are not yet sustainable so that "de novo" systems have to be designed from scratch. This for instance holds for metal carbide and nitride particles, which offer new pathways for metal/base catalysis, but also as record holders in mechanical hardness or magnetization. This is also true for the corresponding borides, which are again new land for chemistry, when rational nanostructures are to be made.

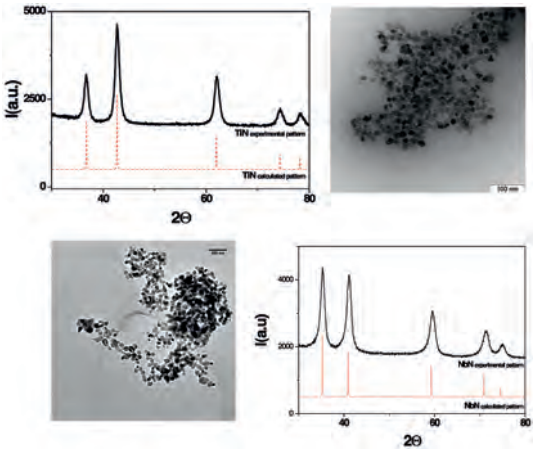

Fig. 1: Experimental (in black) and calculated (in red) WAXS diffraction patterns and corresponding TEM micrograph of TiN (up) and NbN (down) nanoparticles. Estimated sizes by Scherrer's equation: d ~10 nm in both cases

2. Metal Nitride and Metal Carbide

Metal carbides and nitrides nanoparticles are relevant materials for novel energy cycles and more efficient chemical reactions. In general, they possess strength and durability and can show optical, electronic and magnetic properties; as a consequence, they can be applied in many different fields.

Despite that, it is still necessary to establish a general, safe and competitive synthetic procedure to scale up their production for industry.

Recently we set up a simple, inexpensive and versatile route using urea to play a double role of nitrogen/carbon source and stabilizing agent. For the first time, metal carbides were obtained using urea as carbon-source **[3]**. Synthesized metal carbides and nitrides have sizes ranging between 5 and 20 nm in diameter and possess high specific surface area (between 50 and 200 m^2/g), depending on the specific product **(Tab.1)**. Furthermore, they are almost pure and highly crystalline **(Fig.1-2)**. In particular, for metal nitride no larger contents of side products have been found, e.g. amorphous carbon, previously described in related processes as an inevitable companion of these nanostructures.

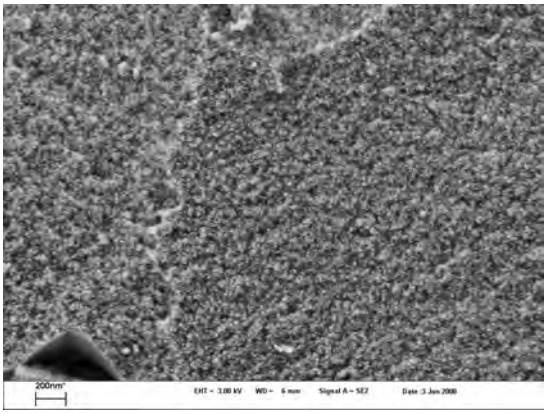

Fig. 2: SEM picture of WC (scale bar: 200 nm) illustrate the large scale homogeneity of the sample and the typical powder texture of very small particles. No structural side products can be seen.

Product	d (nm)	Surface area
TiN	10	~200
VN	15	~200
Fe_3C	30-40	~200
NbC	10	~80
W_2N **WC**	3-5 both cases	~20
Mo_2N **Mo_2C**	20-30 both cases	~50-80

3. Magnetic Nanostructures

In nanoscience, magnetic nanostructures have a special attraction, above all for their use as magnetic data storage, magnetic fluids, magnetic refrigerant and biomagnets.

In particular, iron carbide nanoparticles and nanostructures posses special interest for application such as superior magnetic recording, sensors, catalyst and in new nanoelectronic devices (e.g. in the production of functionalised carbon nanotubes)

With a similar procedure used to prepare MN and MC, highly crystalline Fe_3C have been prepared, simply by mixing an iron salt with 4, 5 dicyanoimidazole (to play the role of C-source). After heating treatment (750°C) under nitrogen flow, a silvery-black, non-corrosive and highly magnetic (when outer fields are applied) powder was obtained (named FeDI) and characterised by TEM and WAXS. TEM measurements **(Fig. 3A)** revealed the presence of fibres while WAXS **(Fig. 3B)** showed the crystallinity of the sample. Nevertheless, the broad peak around 26° (marked with a star) indicates the presence of amorphous carbon. Preliminary experiments showed that carbon contents can be however regulated, simply by playing with external parameter, such as the metal/C-source molar ratio, heating temperature and reaction time.

4. Boron-Based Nanomaterial

Due to their specific properties, boron based materials are attracting great interest **[4]**, e.g. for the development of hard coatings, hydrogen storage devices, catalysts, insulators for electronic devices and sensors. As nanoparticles, they are expected to exhibit modified and/or enhanced properties. Synthesis of boron carbonitrides was made through a sacrificial hard template, (mpg-C_3N_4). Impregnation of the matrix with a borane complex BH_3-amine and thermal post-treatment at 800°C leads to boron (carbo)nitrides of various B, C, N compositions, with B:N = 1.1 molar, irrespective of the initial borane. Use of volatile precursors such as BH_3-*tert*-butylamine, BH_3-dimethylamine and BH_3-trimethylamine results in low carbon content (C:N = 0.4 molar) while the more stable and less volatile BH_3-pyridine complex leads to a high carbon content (C:N = 2.7 molar). XRD patterns indicate that a turbostratic structure is obtained, whatever the boron precursor. This structure is lamellar and related to graphite and hexagonal boron nitride h-BN. SEM and TEM indicate that the resulting materials are composed of nanoparticles with a diameter of ca. 10 nm **(Fig. 4)**, which corresponds to the size of the initial pores which act as nanoreactors for the decomposition of the borane complexes. Moreover, SEM shows the high homogeneity of the sample and no trace of mesoporous carbon was detected by TEM, thus confirming the formation of boron carbonitride nanoparticles.

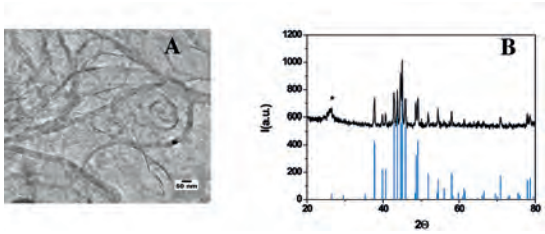

Fig. 3: A) TEM picture of FeDI sample and B) corresponding WAXS pattern (in black). In blue the calculated pattern for Fe_3C.

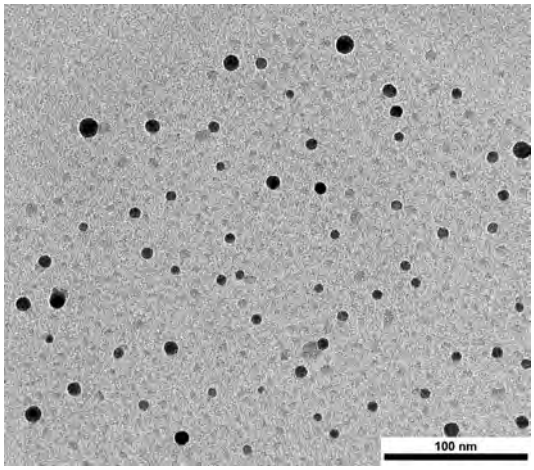

Fig. 4: TEM micrograph of boron carbonitride nanoparticles obtained after treatment for 6 h at 1000 °C of a C_3N_4 mesoporous matrix impregnated with BH_3-tert-butylamine.

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Artificial Photosynthesis

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Natural photosynthesis feeds nearly all life on Earth either directly or indirectly by converting solar energy, carbon dioxide, and water into chemical energy and oxygen, and it has inspired artificial versions of photosynthesis, i.e. the splitting of water into its constituent elements and the conversion of carbon dioxide into organics via sunlight. An important challenge in artificial photosynthesis is to develop efficient, stable, and inexpensive catalysts capable of harvesting visible light. There are countless trials to establish stable systems for this purpose, mostly based on inorganic semiconductors. We are investigating polymeric and organic-inorganic hybrid materials with controlled nanostructures as potential energy transducers for artificial photosynthesis

A. Photocatalytic Water Splitting

Water is an ideal source of hydrogen fuel. The inorganic catalysts developed for water splitting in the past 30 years have been metal-based. We have shown that an inexpensive, stable and metal-free polymeric material, graphitic carbon nitride ($g\text{-}C_3N_4$), **(Fig. 1a)**, is able to catalyze hydrogen production from water with visible light **[1, 2]**.

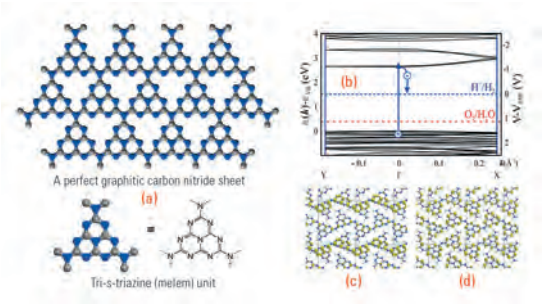


Fig. 1: (a) A perfect $g\text{-}C_3N_4$ sheet constructed from melem units. (b) Band structure for polymeric melon calculated along the chain. The position of the reduction level for H^+ to H_2 is indicated by the dashed blue line and the oxidation potential of H_2O to O_2 is indicated as the red dotted line just above the valence band. (c) The Kohn-Sham orbitals for the valence band of polymeric melon. (d) The corresponding conduction band. The carbon atoms are grey, nitrogen atoms are blue and the hydrogen atoms are white.

This polymer is stable in contact with water even at harsh acidic and basic environments, and can be made from easily available resources in flexible shapes and forms. The $g\text{-}C_3N_4$ sheet is calculated to feature an electronic band structure with band edges straddling H_2O redox potentials **(Fig. 1b)**, and thus it is enabled to photo-split water

H_2 production was achieved by illuminating the mixture of $g\text{-}C_3N_4$ and water in the presence of triethanolamine to short cut the oxygen side of water hydrolysis. This system can produced 0.1-4 umol of H_2 per hour without using any metals, depending on the batch. Notably, a differently modified $g\text{-}C_3N_4$ was also able to photocatalyze oxygen production from water with visible light.

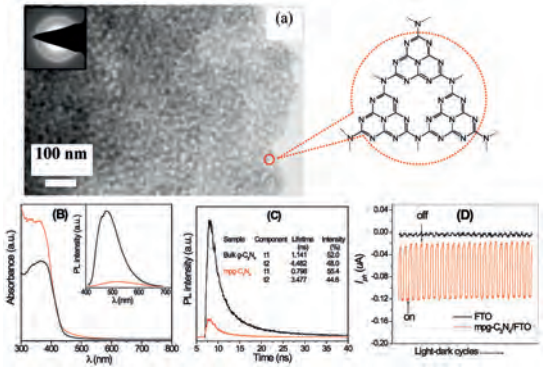


Fig. 2: (A) TEM image of mpg-C_3N_4, showing a 3D porous framework. The stacking distance of 0.332 nm is evident by the intense electron diffraction ring (inset). (B) Optical absorption spectrum and photoluminescence (PL) spectrum (inset) under 420 nm excitation and (C) time-resolved PL spectrum monitored at 525 nm under 420 nm excitation at 298 K for bulk $g\text{-}C_3N_4$ (black) and mpg-C_3N_4 (Red). (D) Periodic on/off photocurrent I_{ph} response of mpg-C_3N_4 electrode in 0.5 M Na_2SO_4 under zero bias in a standard two electrodes photoelectrochemical cell.

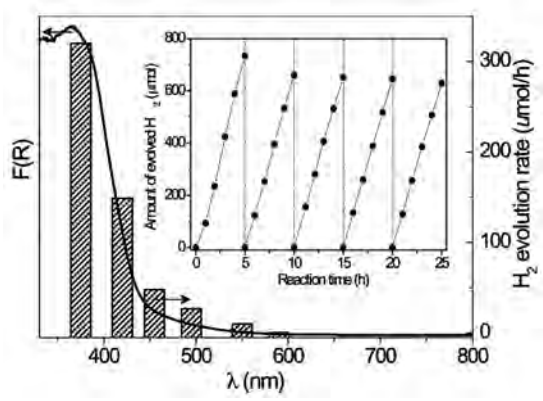
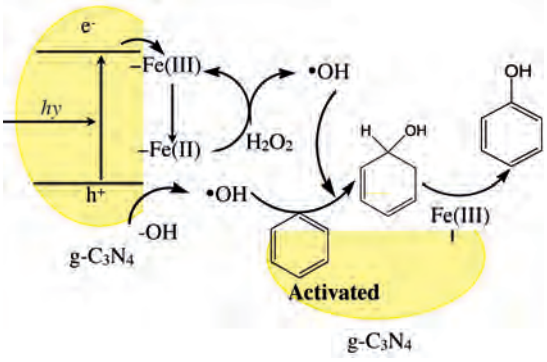


Fig. 3: Wavelength dependence of H_2 evolution rate on Pt/mpg-C3N4. The inset is the stability test for Pt/mpg-C_3N_4 under visible light irradiation (> 420 nm)

We further advance g-C_3N_4 catalysts by protonation **[3]** and also by generating nanopore structures into the polymeric matrix **[4]** to improve their structural and electronic functions for solar energy conversion. The mesoporous g-C_3N_4 (mpg-C_3N_4) feathers unique semiconductor properties along with an open crystalline pore-wall and a large surface area **(Fig. 2)**, which can in principle facilitate mass transfer and enhance light harvesting of the materials. **Fig. 3** shows photocatalytic performance of mpg-C_3N_4 modified with Pt for hydrogen production from the photochemical reduction of water, which is by a factor of 8 higher than that of bulk Pt/g-C_3N_4.

B. Combing Photocatalysis with Organosynthesis

The selective oxidation of organic molecules is of vital importance to chemical industry, especially using clean O_2 and H_2O_2. Natural enzymes such as cytochrome P450, methane monoxygenases, and peroxidase are able to activate O_2 and H_2O_2 at mild conditions for biological oxidations, and thus they are blueprints for the design of environmentally-benign catalysts. A common feature of these natural enzymes is the complexation of iron with tetradentate N_4-donor ligands in π-conjugated macrocyclic molecules. Iron-modified g-C_3N_4 (Fe-g-C_3N_4) features this catalytic structure, which, together with the ability of g-C_3N_4 to adsorb and activate benzene chemically motivate us to use it as an oxidation catalyst for the selective oxidation of benzene to phenol. **[5]**



Scheme 1: The proposed coupling process of visible-light-induced redox catalysis with one-step phenol synthesis by Fe-g-C_3N_4

Fe-g-C_3N_4 is active for the direct oxidation of benzene to phenol using hydrogen peroxide, even at neutral pH without the aid of strong acids or alkaline promoters. By taking advantages of the photocatalytic functions of g-C_3N_4, the yield of the phenol synthesis can be markedly improved. The optimized benzene conversion reached 12% with 96% phenol selectivity (based on benzene) at mild conditions (60 °C, 4 h). This solid-state bioinspired iron catalyst holds great promise for oxidation reactions in synthetic chemistry in general: it nicely combines photoredox catalysis with organosynthesis.

C. Environmental Purification

To design more efficient carbon nitride photocatalysts, it is desirable to extend the light absorption further into the visible spectrum. We show that appropriate amount of metal ions, e.g., Fe^{3+}, Zn^{2+}, and Cu^{2+}, can be included into the matrix of g-C_3N_4 by a simple soft chemical method. The metal components strongly modify the electronic properties of g-C_3N_4 extending the optical absorption to 650 nm **(Fig. 4)**, and render the material with new functionalities such as mimicking metalloenzymes in the activation of H_2O_2. The oxidative degradation of various organic dyes [e.g., rhodamine B (RhB), methylene blue, and methyl orange] can be achieved by using H_2O_2 and Fe-g-C_3N_4. Markedly, the overall efficiency of the process can be enhanced by photo-illumination.**[6]**

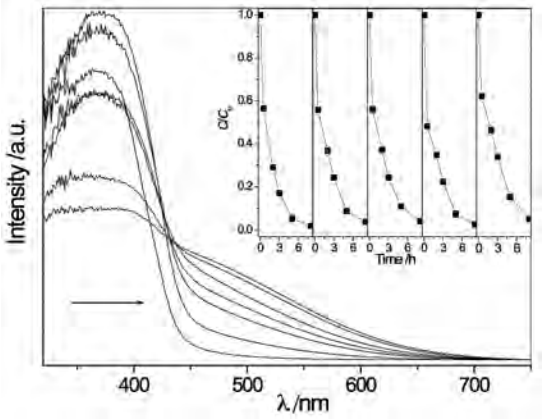


Fig. 4: Optical absorption spectra of Fe-g-C_3N_4 compared with that of g-C_3N_4. Arrow direction: g-C_3N_4, 1%-Fe/g-C_3N_4, 3%-Fe/g-C_3N_4, 5%-Fe/g-C_3N_4, 10%-Fe/g-C_3N_4, 15%-Fe/g-C_3N_4, and 20%-Fe/g-C_3N_4. The inset is cyclic run of RhB (10 μM) degradation by H_2O_2 (0.05 M) catalyzed by Fe-g-C_3N_4 catalyst (40 mg).

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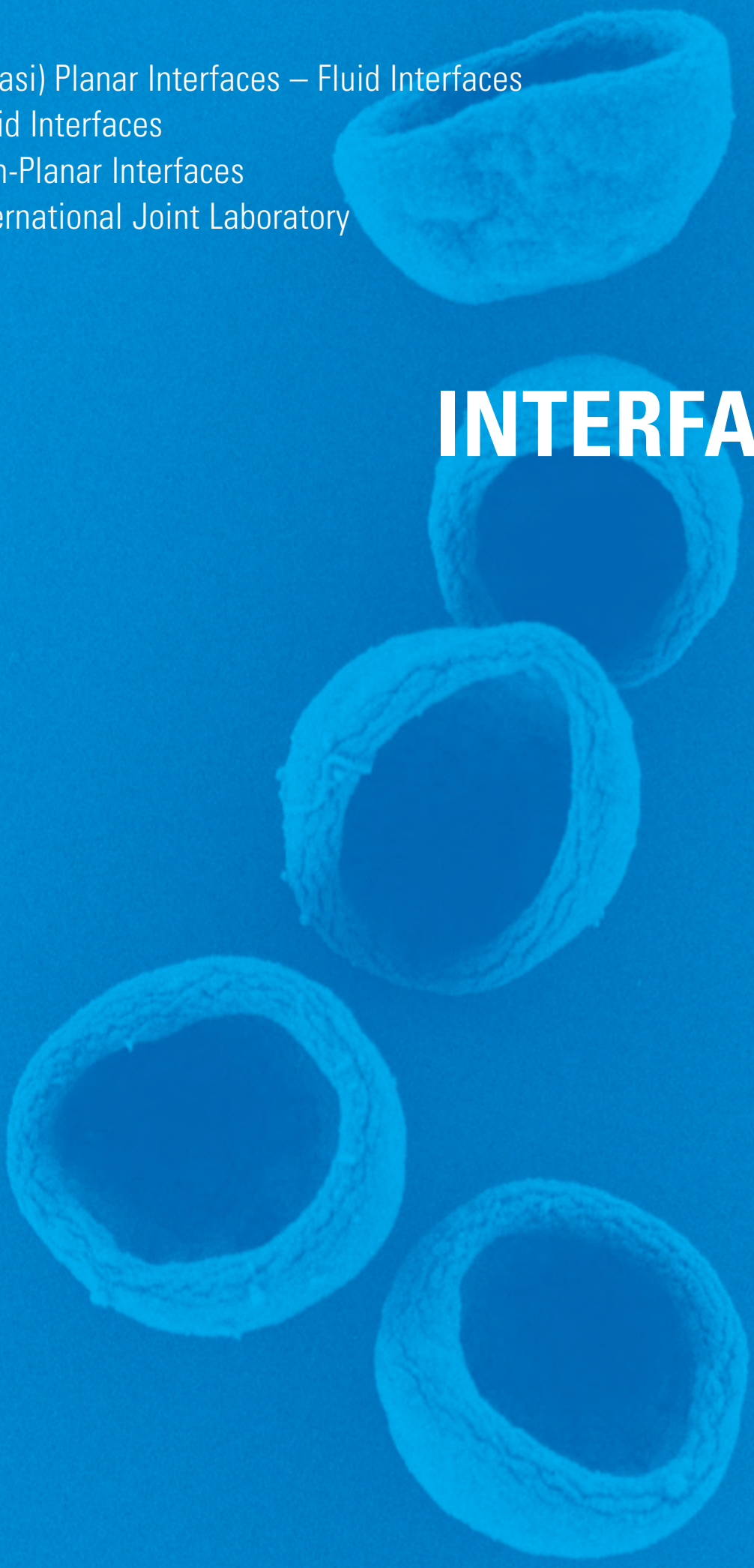
*

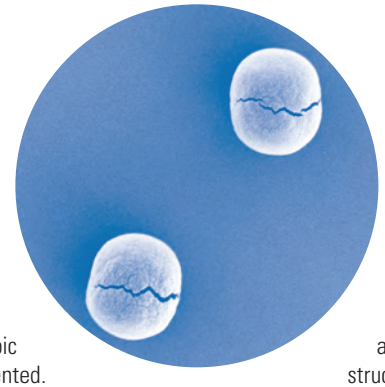
→ (Quasi) Planar Interfaces – Fluid Interfaces
→ Solid Interfaces
→ Non-Planar Interfaces
→ International Joint Laboratory

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. X-Ray fluorescence is introduced to measure the specific ion binding to monolayer surfaces and, surprisingly, monovalent ions like Cs^+ may effectively replace divalent ones (Ca^{2+}). For an antibiotic peptide it is demonstrated how it binds to the membrane to destabilize it. New cationic lipids with high transfection potential are shown to align DNA coupling to an interface. The binding of the enzyme phospoinositide-3-kinase is shown to depend on lipid phase and charge and also its products are miscible in the membrane to a different extent.

The group of *H. Motschmann* has shown by IR-Vis sum frequency spectroscopy that large and polarisable ions adsorb to a water surface in an oriented way and also distort the water structure. Vibrational modes of even highly symmetric molecules are measured, apparently due to the symmetry break encountered at the interface.

The group of *R. Miller* has demonstrated that protein/ surfactant complexes may have different surface activity depending on their stoichiometry. They may be more hydrophobic and replace surfactant at the interface or they may become more hydrophilic and thus be soluble in water. This could be demonstrated by dynamic surface tension studies as well as by shear rheology.

The group of *R. Krastev* has qualitatively explained the unusual drainage velocity of foam films and found a bridging effect for rod-like ions. They managed to prepare asymmetric films of polyelectrolytes suitable for vectorial charge transfer and could arrange layers of magnetic nanoparticles. These, due to aggregation showed response measured by spin-polarized Neutron reflectivity.

The group of *H. Riegler* has shown for C60 droplets that line tension may affect the shape of adsorbed aggregates. For alkanes as model adsorbates with exclusively van-der-Waals interactions, the melting point reduction at a surface could be converted into interaction potentials. It was shown to quantitatively differ comparing alkanes with fatty acids. This group is now also extending their studies on controlled nucleation and growth at surfaces towards nanostructured films that may become relevant for organic photovoltaics.

II. 2 Non-Planar Interfaces

The complexation of bisterpyridines and metal ions studied in the group of *D. Kurth* was shown to be highly dynamic. Combining analytical ultracentrifugation (coop. with *H. Cölfen*, Coll. Chem.) and simulations of rate equations (coop. with *T. Gruhn*, Theory) the unusual dependence can be explained almost quantitatively. The polymer length was also found to differ in solution and at interfaces which can be qualitatively understood (coop. with *J. Raabe*, Humboldt Univ.)

The group of *D. Shchukin* has been extremely successful in developing coatings with feedback activity. This was made use of in anticorrosion coatings and is also promising for antifungal coatings and containers delivering energy on demand. The ideas and experiments have become most fruitful that the group attracted much funding, including direct industry funding.

Major activity of the group of *D. Wang* concerned the funcionalization of nanoparticles to switch their surface activity. Meanwhile they could show the reversible phase

transfer of metallic and magnetic nanoparticles. Also their aggregation could be reversibly changed via temperature and salt enabling switching on and off collective optical and magnetic properties.

It was shown in the former groups of *A. Fery* and *G. Sukhorukov* that glass transitions can be induced in polyelectrolyte multilayers via salt and temperature (20-50°C), and in the high temperature state the film is permeable for large and small molecules. Incorporating metallic nanoparticles into these films tremendously increases IR absorption, due to the low heat conductivity of the surroundings temperatures may by locally increased by up to 100°C, and this hot spot can be confined to some 10 nm. This is quantified by simulations and experiments in the group of *A. Skirtach* using this for remote and controlled release of drugs inside cells and for hot nanoembossing.

In the International joint laboratory with the Chinese Academy of Science led by *Junbai Li* heating of capsules followed by cooling is used to anneal defects such that they become impermeable to small drugs at room temperature. These capsules have been equipped with specific recognition sites to enable transport by molecular motors. Here capsules are good "model cargos" to understand the mechanisms because size and surface can be manipulated in a defined way.

T. Nakanishi has taken over the leadership of the joint laboratory with the "National Institute for Materials Science" in Tsukuba. He used fullerenes with attached aliphatic tails as building blocks to obtain hierarchical structures with lamellae and micelles as basic units. He thus could obtain stable ultrahydrophobic coatings and films with high (two-dimensional) charge carrier mobility. In addition the flower-like structures could be templated to obtain metal surfaces with high specific area suitable for electrochemical and Raman studies.

The results of the joint laboratory (Laboratoire Européen Asscie (LEA) with the institute of separation chemistry (ICSM) in Marcoule on sonochemistry, active since 01.01.2008 on sonochemistry are listed in *D. Shchukin's* report who also leads this laboratory. The success, preparing new nanostructures with specific catalytic, optical and encapsulation properties by this highly nonequilibrium process is documented in many publications. Lacking is the mechanistic understanding for which optical experiments of single and multi-bubble luminescence are now set up.

III. Future Development

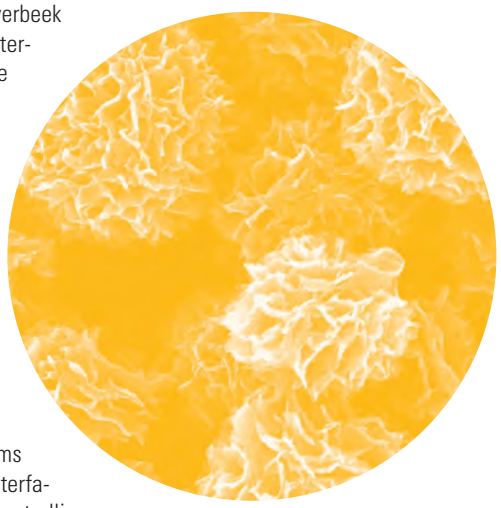
Major changes of staff in the last 2 years have been:

- *R. Krastev* has moved as a group leader to the institute of natural and medical science at the Univ. Tübingen. His work on foam films will be terminated with a student and a post-doc finishing this year. The work on multilayer films will be continued in collaboration with the aim of establishing bioresponsive and magnetoresponsive films.
- *H. Motschmann* accepted the offer of a professor position at Univ. Regensburg. His group has moved there taking with them the equipment for nonlinear optical spectroscopy.
- *D. Kurth* has moved as professor to Univ. Würzburg. The activities of his group will be terminating with the last two graduate students finishing.

Since I intend to retire in 2011 plans for the future are dominated by the need to develop a career of scientists, not having permanent positions in the institute, at some attractive places outside. This basically means strengthening cooperations and attracting funding that people could work in outside laboratories. Thus responsive multilayer films will be pushed within the Campus project on "Bioactive Surfaces", and hydrogels are central in a collaboration with TU Berlin within the Excellence Center on Catalysis. Responsive nanoparticles are in the focus of collaborations with medicine (Charité), biochemistry (Univ. Münster) and pharmacy (Univ. Saarbrücken). Self-repairing coatings have already developed very well in collaborations and funding and will provide many opportunities for the scientists involved. I expect this also for the started activities on sonochemistry where we would like to introduce more surface science and understanding and later transfer knowledge and scientists to France.

With these collaborations mentioned above the funding and the scientific output could be maintained at a high level as well as the size of about 80 persons. It will have to be reduced by a factor of 2 within the next 2 years, and so the main challenge will be to help the many highly motivated co-workers find attractive positions.

Major awards have been given to *T. Nakanishi* and to me in person. I received the Overbeek medal of the European Colloid and Interface Society in 2007, will obtain the Wolfgang-Ostwald award of the Kolloid-Gesellschaft in 2009, the most senior awards of both societies, and in 2008 a honorary doctorate of Univ. Montpellier 2.



My colleagues are continuing their efforts to continue having a department of interfaces with a new director following me. The success, however, is still uncertain. Obviously I would also be very disappointed if they would not succeed in view of the many interesting problems and the fundamental importance of interfacial science for understanding and controlling any hierarchical structure. On the other hand our activities were not confined to one institute and one country and therefore it is the recognition world-wide which counts and which persists beyond our scientific life time. There have been many co-workers in the department working with pleasure and developing their career in many countries, and therefore the knowledge is not only on paper but also in heads, the most important know-how transfer.

Helmuth Möhwald
Director of the Department of Interfaces

Langmuir Monolayers as Model Systems to Study Interactions at Interfaces

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1974: Diploma, Biophysics (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)

Determining structure/function relations for proteins/peptides and lipids requires a milieu that mimics the interfacial environment in which the molecules function. Monomolecular films at the air/water interface are membrane model systems which can be easily varied in terms of lipid composition, lipid lateral packing density, surface pressure and area exposed to the medium. The interactions of dissolved biomolecules with the membrane model interface can change the lipid packing density. On the other hand, lipid structural properties can dictate the adsorption behavior of proteins/peptides. During the last years we have concentrated our efforts on ions **[1, 2]**, DNA **[3, 4]**, enzymes **[5-8]** and peptides **[9-11]** at interfaces.

Ion Specific Effects

The total reflection x-ray fluorescence (TRXF) technique has been developed to be a truly simple tool for elemental analysis within the electrical double layer (EDL) near charged monolayers at the air/water interface (cooperation with Dr. V.L. Shapovalov, IPC RAS Moscow, Russia). The vast majority of counterions is concentrated in the thin inner part of the EDL irrespective of the electrolyte concentration in bulk. Using highly charged monolayers, univalent Cs^+ is quite competitive with divalent Ca^{2+} and Ba^{2+} in the formation of the EDL (which contradicts the classical Gouy-Chapman model). If the univalent/divalent ion ratio in bulk is 9:1, the corresponding ratio in the EDL is ca. 1.5 for Cs^+/Ca^{2+} and 0.5 for Cs^+/Ba^{2+}, whereas the model predicts 0.14 only. Bearing in mind packing density limitations, these values are consistent with a series of sizes for hydrated ions: $Cs^+ << Ba^{2+} < Ca^{2+}$ **[1, 2]**.

TRXF was also used to determine the protonation rate of new compounds designed for versatile DNA delivery systems. The head groups of these cationic lipids, represented by monoamines or oligoamines, can be charged or uncharged in dependence on the environmental pH. Since their pK values are unknown, the 2D concentration of bromide counterions was estimated by comparing the fluorescence intensity with that of DODAB monolayers as a reference **(Fig. 1)**.

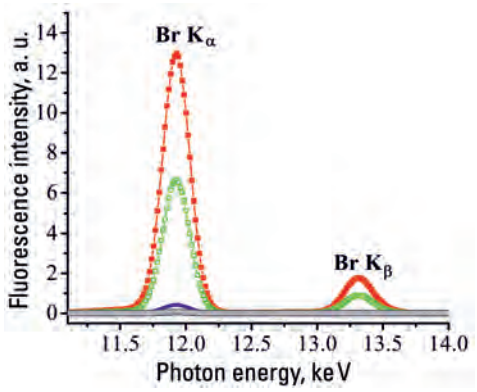

Fig. 1: Selected X-ray fluorescence spectra of the lipid monolayer at 40 Å²-molecule⁻¹ on Br^- containing subphases at pH 3 (■), pH 6 (□), pH 8 (●) and pH 11 (○).

The monolayers of all studied compounds are completely uncharged at pH values above 10. The influence of the monolayer packing density on the protonation properties is clearly shown **[3]**.

Lipids for Gene Transfection

In order to obtain more effective and safer liposome-based gene transfection systems, new cationic lipids have been synthesized in the group of Prof. B. Dobner (University of Halle). The new lipids were studied in 2D as well as 3D systems. The results show clear differences in structure and phase behaviour in dependence on the subphase pH due to protonation or deprotonation of the lipid head group. The packing properties of the molecules in mono- and bilayer systems are very similar. DNA couples to the lipid monolayers at low as well as at high pH, but in different amount. The DNA coupling leads to an alignment of adsorbed DNA strands **(Fig. 2)**. The distance between aligned DNA strands does not change much if the lipid layer is condensed **[4]**.

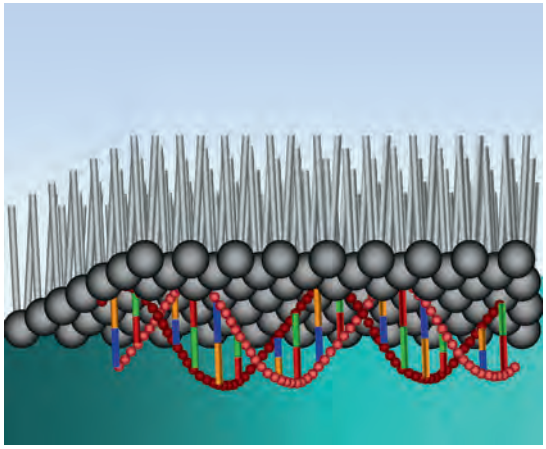

Fig. 2: Molecular model of DNA ordering at the monolayer of the novel cationic lipids.

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Phosphoinositides and Phosphoinositide 3-kinase γ

Phosphatidylinositol and its phosphorylated derivatives play crucial roles in a broad range of signal transduction processes. To shed light on processes that lead to the formation of phosphoinositide-enriched microdomains, mixed monolayers were investigated **[7]**. DOPtdIns is capable to mix partially with condensed DSPC and to form mixed crystals which differ significantly from those formed by pure DSPC. DOPtdIns(4,5)P_2 in mixtures with DSPC is to a much larger extent phase separated **(Fig. 3)**. In biological systems, an enzymatic phosphorylation of phosphatidylinositol in mixed domains may cause their insolubility in ordered PC areas and leads to a cooperative reorganization of the host lipid membrane.

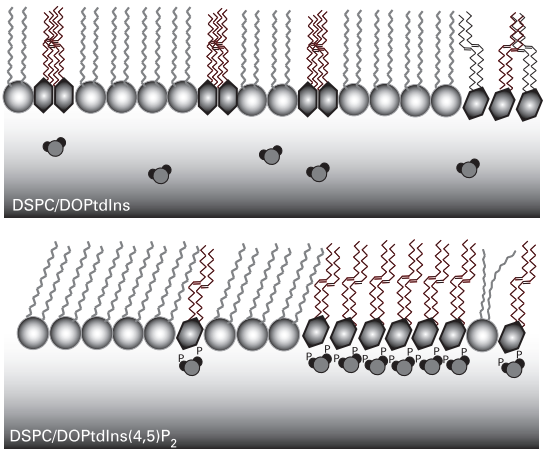

Fig. 3: Scheme of the molecular arrangement in the investigated mixtures. The non-phosphorylated inositides (DOPtdIns) are partly distributed within the condensed DSPC layer (top) and are able to change the orientation of the DSPC molecules. Oppositely, the highly charged DOPtdIns(4,5)P_2 is mostly phase separated (bottom). The water molecules interact with the DOPtdIns(4,5)P_2 and stabilize this phase.

The recruitment of phosphoinositide 3-kinase γ (PI3Kγ) to the membrane is the crucial requirement for the initiation of, e.g., inflammation cascades by second messenger production (cooperation with Prof. R. Klinger, University of Jena). The adsorption behavior of GST-PI3Kγ to non-substrate as well as substrate lipids was investigated by Infrared Reflection Absorption Spectroscopy (IRRAS). The enzyme does not interact with condensed zwitterionic or anionic monolayers. However, it can penetrate into uncompressed fluid monolayers. Protein affinity for the monolayer surface is considerably increased when the lipid has an anionic head group and contains an arachidonoyl fatty acyl chain in sn-2 position **[8]**. The protein adsorption has a condensing effect in phosphoinositide monolayers.

Antimicrobial Peptides

Over recent decades a broad spectrum of antimicrobial peptides (AP) has been identified as a native line of defense in animals, plants, and also in single-cell organisms. They are also of great scientific interest because they are promising candidates for the development of novel therapeutics. We have studied the interactions of APs with different surfaces using a large variety of modern methods (cooperation with Dr. J. Andrä, Research Center Borstel). NK-2 is an antimicrobial peptide derived from the cationic core region of porcine NK-lysin. It adopts an unordered structure in water, buffer, and in the presence of monomeric cationic and non-charged amphiphiles. However, it forms a stable α-helix in 2,2,2-trifluoroethanol (TFE) and in micellar solutions of anionic, cationic as well as nonionic amphiphiles. NK-2 is surface active and forms a Gibbs monolayer at the air/buffer interface. In contrast, no adsorption was observed if NK-2 is dissolved in water. During the adsorption process in buffer solutions, NK-2 undergoes a conformational transition to an α-helix which lies flat at the interface. This is confirmed by X-ray reflectivity (XR) measurements **(Fig. 4)** revealing that the adsorption layer of the peptide NK-2 possesses a thickness of 17 Å **[10]**.

Figure 7

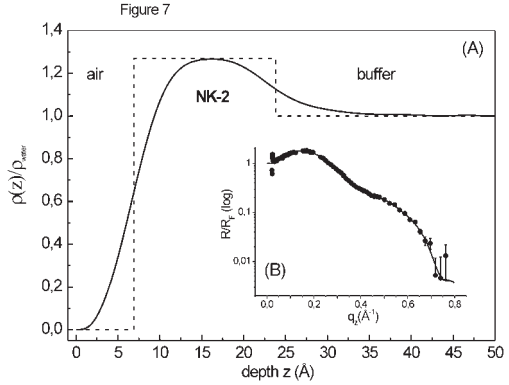

Fig. 4: Specular X-ray reflectivity normalized by the Fresnel reflectivity, $R(q_z)/R_f(q_z)$ (inset B) and the corresponding electron density profile (solid line in A) of NK-2 adsorbed at the air/buffer interface. The dashed lines represent the one-box model used to describe the electron density profile. Solid line in panel B is the best fit using a model-independent approach.

The peptide film is very stiff and can be compressed if trapped at the water surface. In contrast, the secondary structure (α-helix) of the AP dicynthaurin is maintained upon adsorption. XR and IRRAS showed the destabilization of the condensed phase of a pure DPPG monolayer. Penetration of the peptide was found to be pressure dependent. The results suggest that the APs are able to adsorb to PG-rich cytoplasmic membranes of bacteria and alter membrane integrity **[11]**.

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Thin Soft Films

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We study the properties of matter when it is organised in thin layers. These are layers with a thickness not more than 100 nm. Interactions between the surfaces are active in such systems and govern their properties to large extent. Such thin layers can be used to perform model studies on the interactions in the colloidal systems or to study the organisation of different species in two dimensions (2D). We use two systems for our studies – thin free standing (foam) films and polymer (polyelectrolyte) films on solid support.

Foam films

Foam films fascinate with their wonderful play of colours, but they also have been used for long time to study the strength of interactions between fluid (gas/liquid or liquid/liquid) interfaces. Such films can have a thickness of only few nano meters, but areas up to few square meters. This makes them easy for preparation with well reproducible molecular flat surfaces. The foam films consist of an aqueous core sandwiched between two adsorbed surfactant layers. The films are generally prepared from a drop of an aqueous surfactant solution. Under the action of capillary pressure 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. First common black films (CBF) are formed during the thinning process. When the electrolyte concentration in the film forming solution is properly chosen, thinner Newton black films (NBF) are formed in the CBF. The transition from CBF to NBF is a stochastic process and its probability depends on the strength of double layer electrostatic repulsion between the film surfaces.

Effect of the Shape of the Ions on the Electrostatic Interactions

(together with K. Bohinc, Lublijana)

The forces operative between the film interfaces according to the classical DLVO theory are expressed as disjoining pressure (Π) in the case of thin films. Π has an attractive van der Waals component Π_{vw} and a repulsive double layer electrostatic component Π_{EL}. The strength of Π_{EL} decreases strongly when ions are added to the aqueous phase of the film. This makes the films thinner and in extreme case they can rupture. Π_{EL} depends also strongly on the charge of the added ions. We focused our attention on the influence of the shape of the ions on Π_{EL}. We measured the thickness of films prepared from the non-ionic surfactant Dodecyl Maltoside (C12G2) in presence of spermidine and compared the results to those obtained in presence of NaCl. Spermidine is a three valent rod-like ion. The films prepared in presence of spermidine have the same equilibrium thickness as that of the films in presence of NaCl. There is no difference in the velocity of film thinning also. The major difference is that the probability of formation of NBF in the thicker CBF is much faster in the case of films prepared with spermidine **(Fig. 1)**. The results show that the presence of rod-like ions in the solution facilitates the transition of CBF to NBF most probably by "bridging" the opposite film surfaces.

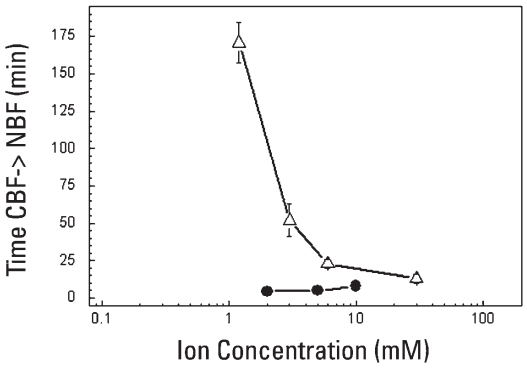

Fig. 1: Time for formation of NBF in the thicker CBF as a function of the ion concentration. Δ - in presence of 0.2 M NaCl; ● - in presence of spermidine with equivalent number of charges.

Foam Films from Ionic Liquids

Ionic liquids (IL) are liquids with the nature of salts. They are composed of cations and anions only. Besides non-volatile, ILs are non-flammable, thermally stable and structurally tuneable. All of these advantages make them a promising replacement for the traditional volatile organic solvents. We proved if stable foam films can be prepared from pure ionic liquid. Studying the interactions between the surfaces of the films made from IL we aim to shed more light on their structure near interfaces. We studied films formed with the IL $[EMIM]^+BF_4^-$. Formation of stable foam films only from IL was not possible. Addition of surfactant (e.g. 0.1 mM Brij35) was necessary to stabilise the films. Further studies are necessary to conclude if the ordering of the IL near interfaces as already reported may stabilise the films.

GISAXS from Foam Films

(cooperation P. Müller-Buschbaum, München)

Many experiments with foam films study the organisation of matter normal to the film surface. GISAXS allows to study the in-plane structure of the films and to probe organisation of nano defects (e.g. distribution of nano particles) in it. We performed first GISAXS experiments with foam films prepared from solutions of C12G2 and NaCl. Nano sized metal particles with a diameter of ca. 12 nm were added to the film forming solution. The scattering image of the 2D position sensitive detector at the beam line BW4 at DESY Hamburg is shown in **Fig. 2.** Well pronounced satellite reflections are visible which confirms formation of ordered structures in the plane of the film. This result opens possibilities to use foam films to organise small particles in well ordered structures.

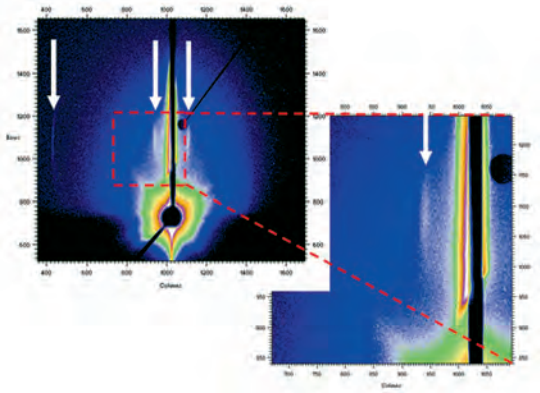

Fig. 2: GISAXS images from foam films which contain metal particles with a diameter of ca. 12nm.

Polyelectrolyte Films on Solid Support

We aimed to understand the organisation of polyelectrolytes (PE) in multilayers (PEM) and thus to be able to use them to build complex materials. We studied the effect of the first PE layer which assures the contact between the film and the support, the effect of the film post treatment and the film preparation (dipping vs. spraying) on the film thickness and density. We found that the ordering of nanoparticles on/in PEM depends on the treatment of the films. The NP were uniformly distributed in freshly prepared samples while only a highly concentrated layer of NP was formed when the PEM were exposed to elevated temperature after their preparation. The observed effect was correlated to glass-melt transitions of the PEM. We have studied magnetic response of magnetite-PEM composites. We found magnetic response which proved formation of the nano composites with appropriate high concentration of magnetic nanoparticles **(Fig. 3)**.

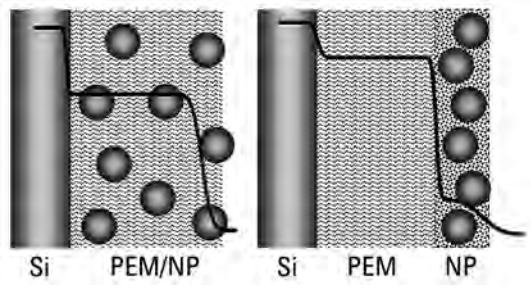

Fig. 3: Formation of composite films of PEM and magnetite nanoparticles. Left – fresh prepared samples; right – after temperature treatment. The lines present the change in the neutron scattering length density in the samples. .

Formation of asymmetric lipid layers was successful applying only one single lipid bilayer from the phospholipid DMPE and using its sensitivity to the pH of the solution. The bilayer was formed on PEM prepared with two strong polyelectrolytes - PSS and PDADMAC. The DMPE was always deposited onto the PEM cushion terminated with positively charged PDADMAC. The surface charge of the DMPE-coated film depends on the pH of the buffer solution. Formation of PEM could be continued on the top of the lipid bilayer by tuning the head group charge of the DMPE. An asymmetric structure of the PEM/DMPE/PEM "sandwich" was created in the case where anionic PSS was used as the first layer of the subsequent PEM. In this system, the DMPE lipid membrane was constructed as a charge asymmetric barrier sandwiched in the interior of the PEM films.

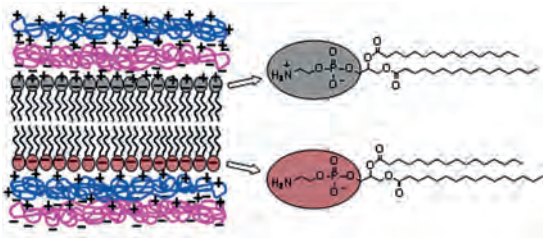

Fig. 4: A schematic structure of the PE multilayer architecture of sandwiched asymmetric lipid bilayers.

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Replacement of Proteins by Surfactants from Adsorbed Interfacial Layers

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Thermodynamic and kinetic adsorption theories for mixed interfacial layers were derived by us recently, and the resulting equations of state, adsorption kinetics and dilational rheology were published for example in **[1]**. It was found for protein/surfactant mixed solutions that their adsorption at liquid interfaces is based on a combination of complex formation between protein and surfactant molecules and competitive adsorption between the formed complexes and free (unbound) surfactant molecules. The complexes are formed due to ionic and/or hydrophobic interactions between the different species. For non-ionic surfactants the complexes are formed exclusively on the basis of hydrophobic interactions between the surfactant's hydrocarbon chain and the hydrophobic domains of the protein **(Fig. 1,** top**)**. This results in more hydrophilic complexes which are less surface active than the original protein.

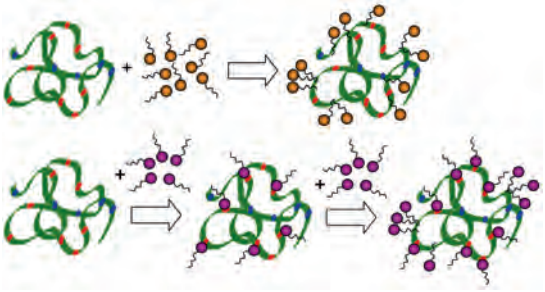

Fig. 1: Illustration of the interaction of surfactants and a protein molecule in aqueous solution; top – non-ionic surfactant, bottom – cationic surfactant; the red and blue areas on the protein chain represent negatively and positively charged domains, respectively.

The addition of ionic surfactants to a protein solution leads to complexes via the stronger ionic interaction between the charged surfactant head groups and the oppositely charged domains of the protein molecule. This process leads to increased hydrophobicity and hence higher surface activity of the complexes as compared to the original protein. Once the available charges in the protein chain are compensated, a further addition of surfactant molecules leads to hydrophobic interactions, hydrophilising the complexes, which become consequently less surface active **(Fig. 1,** bottom**)**. The interaction with surfactants causes conformational changes of the protein molecules in the bulk and at the interface.

The question whether proteins can be replaced by surfactants at an interface can be answered on the basis of this general mechanism. Experiments have been performed with various proteins, such as lysozyme **[2, 3]**, β-casein (BCS) **[4, 5]**, β-lactoglobulin (BLG) **[6]**, and enzymes **[7]** in interaction with non-ionic surfactants like decyl and dodecyl dimethyl phosphine oxide (C_{10}DMPO and C_{12}DMPO), fatty acid or monoglycerides, and ionic surfactants like sodium dodecyl sulphate (SDS) and dodecyl trimethyl ammonium bromide (DoTAB) at the water/air **[2-5]** and water/oil interfaces **[6, 7]**.

Experimental surface tensions for mixtures of 7×10^{-7} mol/l lysozyme/SDS at different SDS concentrations are shown in **Fig. 2**. The isotherm for individual SDS solutions is also given for comparison. The curves correspond to calculations using the models given for example in **[1]**. The thin solid line corresponds to the formation of complexes by one protein molecule and 8 SDS molecules, assuming that the surface activity of the complex is the same as the one of the original protein molecule, while the bold solid line corresponds to an increase in surface activity of the complex by a factor of 10 **[2]**.

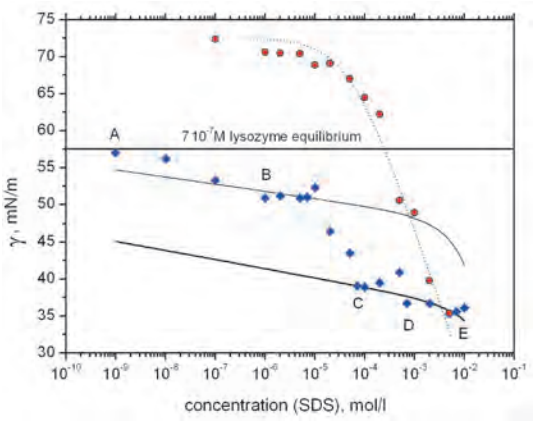

Fig. 2: Surface tension isotherm for SDS (◆) and 7×10^{-7} mol/l lysozyme + SDS (●) at the air/water interface, the lines are calculated curves as discussed in [2]

These two theoretical curves represent a kind of frame within which the experimental data are found. In the concentration range between the points A and B, electrostatic binding of SDS to the protein is very low in view of the low SDS/lysozyme ratio. At SDS concentrations higher than 10^{-6} mol/l (beyond point B) the electrostatic bonding of SDS becomes significant and the complexes are hydrophobised, resulting in an increased surface activity **(**BC range in **Fig. 2)**. At pH 7 the net charge of lysozyme is about 8, so that charge neutralization can be assumed at about 5?10?5 mol/l SDS. Further increase in the SDS concentration leads to the hydrophilisation and stepwise solubilisation of the complex caused by the dominating hydrophobic interactions (CDE range); however, this does not result in a further significant surface tension change for the mixed solution.

The two measured isotherms, for the mixture and the pure SDS, overlap close to the critical micelle concentration of SDS (5×10^{-5} mol/l in buffer) suggesting an adsorption layer built mainly by free SDS molecules. The given explanations are confirmed by a decrease in the foam film thickness, by a decreased adsorbed amount, as measured by ellipsometry, and a change in the dilational rheological behaviour, which were all observed in the same concentration range **[3]**.

The situation is changed when the protein molecules are pre-adsorbed and the adsorption of surfactants is made subsequently, as it was discussed recently **[4]**. In such a sequen-

tial adsorption process it is assumed that the proteins adsorb kinetically irreversibly, i.e. stay at the interface when all protein molecules are replaced from the subphase. Addition of the surfactant after another subphase exchange leads to a first contact and complex formation with the protein only at the interface.

In **Fig. 3** the dynamic surface tensions are shown as obtained in bulk-exchange processes with different surfactant concentrations, using a BCS layer pre-adsorbed from a 10^{-6} mol/l solution. The higher the surfactant concentrations, the lower are the final surface tensions. BCS, like most proteins with a molecular weight between 10 kDa and 30 kDa yields surface tensions not significantly lower than 50 mN/m. Thus, from the observed values, even below 30 mN/m, we can conclude that the surfactants displaced most of the protein molecules from the surface layer due to complexation and a subsequently strong competition.

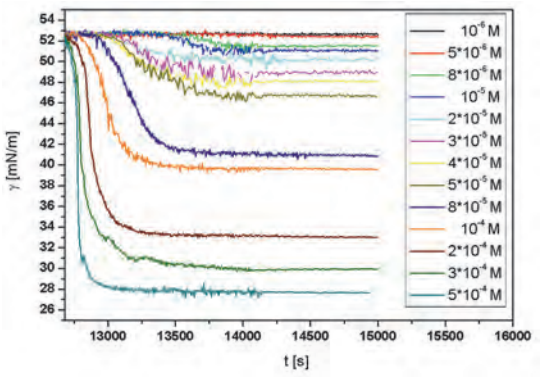

Fig. 3: Dynamic surface tensions measured during the drop-bulk exchange process measured for a sequential adsorption at different C_{12}DMPO concentrations at a fixed BCS concentration of 10^{-6} mol/l [4]

In **Fig. 4**, surface tension curves are shown which correspond to another subphase exchange, replacing the previously injected C_{12}DMPO molecules by a pure buffer solution (washing-out). In case, the surfactant has displaced the protein from the interface, we should arrive at a surface tension close to that of water, because any surfactant molecule desorbs immediately into a pure buffer solution. As one can see, the higher the injected C_{12}DMPO concentration was, the closer are the final surface tensions to that of pure water, i.e. the more proteins were displaced from the interface by the surfactant molecules.

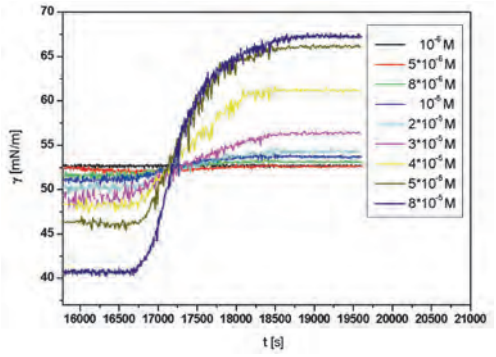

Fig. 4: Dynamic surface tensions measured during the drop-bulk exchange processes after sequential adsorption experiments at different C_{12}DMPO concentrations and subsequent exchange with a buffer solution (washing out); all experiments were performed at an initial BCS concentration of 10^{-6} mol/l [4]

The displacement of protein molecules at the interface by increasing amounts of surfactants added to the bulk solution was also studied at the water/oil interface (water/hexane **[6]** and water/triglyceride **[7]**). As shown in **Fig. 5** for mixed BLG/SDS solutions, the adsorbed amounts of BLG are much higher at the water/hexane than at the water/air interface, while for the SDS the opposite is obtained. For SDS concentrations above 10^{-4} mol/l, the surface tensions for the mixtures at both interfaces decrease until the curves merge with the isotherm of the pure SDS and are identical at the CMC. Studies of dilational rheology indicate a decrease of the visco-elastic modulus at both interfaces which can again be attributed to the presence of an increasing quantity of surfactant molecules in the adsorption layer due to the replacement of the complexes **[6]**.

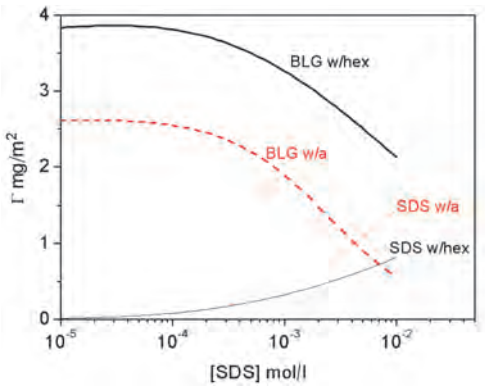

Fig. 5: Interfacial concentration Γ of BLG and SDS adsorbed at the water/air (dash line) and the water/hexane (solid line) interface, calculated from γ(c) isotherms [6]

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Ion Distribution at Interfaces

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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 combination of the Boltzmann distribution with the Poisson equation leads to a non-linear second order differential equation for the electric potential. 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 unrealistic 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 extensions 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 pure 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 aqueous electrolyte solution interface is based on a thermodynamic analysis of the equilibrium surface tension isotherm. 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. 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 to the Gibbs equation. Therefore, direct experimental observations of molecular structure and energetics of ions in the interfacial region are required.

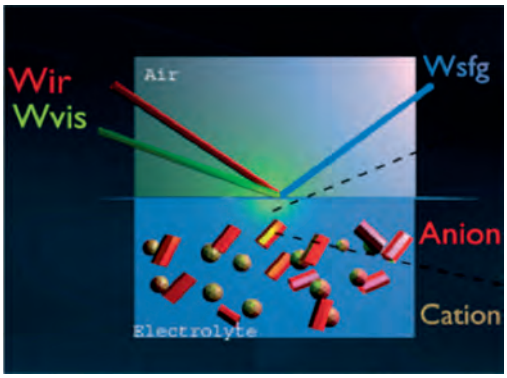

Fig. 1: Scheme of a SFG experiment: The spatial and temporal overlap of an infrared and visible laser pulse generates light at the sum frequency.

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

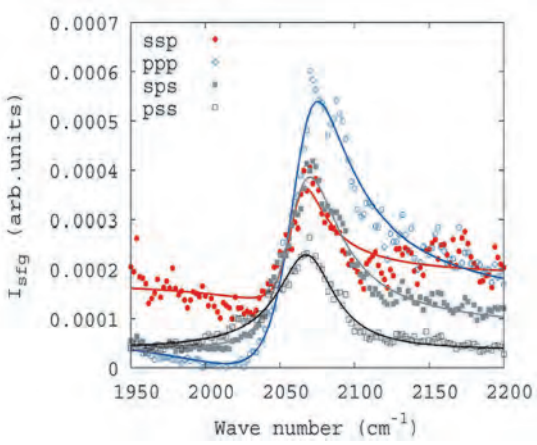

Fig. 2: Vibrational sum frequency spectra showing the CN stretch of the thiocyanate anion for 1 ~M potassium thiocyanate solution. The points and continuous lines represent the experimental data and fits respectively.

Polarization dependent measurements have been used for a determination of the orientation of the pseudo-halide anion. The combined data gives a picture of the interfacial architecture on a molecular scale. We believe our current study contributes towards better understanding of this biologically relevant chaotropic 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.

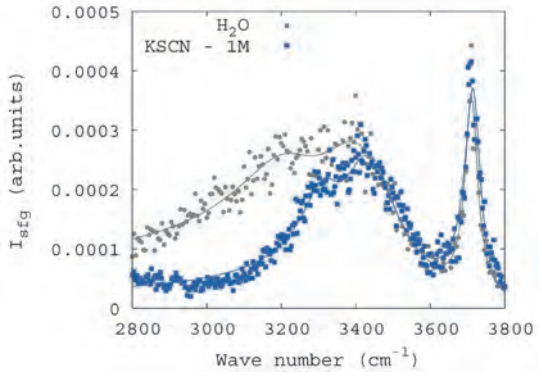

Fig.3 Vibrational sum frequency spectra of water and 1 ~M potassium thiocyanate solution. The points and continuous lines represent the experimental data and fits, respectively.

As a consequence of its chaotropic nature, the favourable adsorption of the thiocyanate anion at the interface perturbs the hydrogen bonded network and distorts it significantly which becomes more prominent at higher concentration. In particular, the spectra show considerable enhancement of liquid-like ordering occurring at 3450 cm^{-1} and vanishing ice-like feature at 3200 cm^{-1} in agreement with recent reports on large and highly polarisable anions. In addition, the feature at 3320 cm^{-1} which is attributed to the tetrahedral coordination of water increases with concentration. The geometry of the thiocyanate anion (linear), higher polarizability and its low hydration tendency in addition to its orientation, clearly restructures the water network at the interface. Molecular dynamics simulation would shed some light on the density of the dominant species at the interface and the nature of ion-water interactions by constraining the orientation of the ion. Understanding of this mechanism of hydration will be crucial to address the more complex protein-aqueous electrolyte interfaces concerning the "salting in" and "salting out effects", specifically to identify whether direct ion-protein local binding or mediation through interfacial water are responsible for such processes.

The reported features are not a peculiarity of the thiocyanate. For instance we could prove that potassium azid behaves in a very similar fashion. Another interesting system which we recently studied is the potassium hexacyanoferrat **(Fig. 4)**. This inorganic complex possesses octahedral symmetry Oh. A normal coordinate analysis reveals that this model system does not possess SFG active modes.

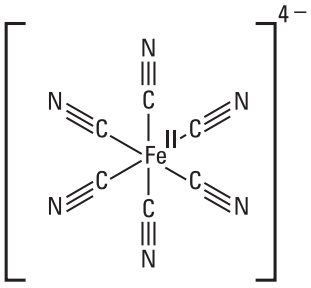

Fig. 4: Structure of the hexacyanoferrate ion

However, we detect a strong IR-VIS SFG signal for the ssp polarisation combination in reflection mode at the air-water interface **(Fig. 5)**. The asymmetry of the interface apparently deforms the octahedral coordination shell from oh to C4v symmetry and distinct vibrational modes can be observed in the spectra.

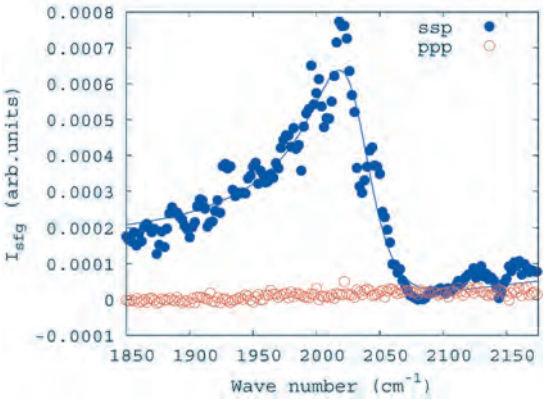

Fig. 5: Vibrational sum frequency spectra of the hexacyanoferrate ion at the air/water interface for two different polarizations.

This work must have also impact on atmospheric research and it is on the agenda to explore this. It is well established that some electrolytes at sufficiently high concentration can inhibit bubble coalescence relative to the pure liquid. V. Craig et al. classified electrolytes according to their coalescence behaviour based on empirical cation and anion assignments. The mechanism behind electrolyte inhibition, as well as the salt differentiation, is not understood but must be related to the internal organization at the interface.

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Phase Transitions, Nucleation, and Transport Phenomena at Solid/Air Interfaces

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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, (Max Planck Institute of Colloids and Interfaces, Potsdam)
1996: Habilitation, (Mainz University)
Thesis: Interface-induced structure formation through Langmuir-wetting in monomolecularly thick organic layers on planar solid surfaces

Aims:

Understanding of solid/liquid phase transitions, nucleation, structure formation, transport phenomena, and wetting properties of confined systems, in particular molecularly thin films at solid/air interfaces.

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. in microfluidics, nanotechnology, sintering, etc.

Work:

In the last two years we gained new insights into:

1.) *How the surrounding interface affects the solid/liquid phase transition behavior of adsorbed solid aggregates.* We find that the wetting properties of surrounding interfaces can considerably lower (up to more than 50°C!) the solid/liquid phase transition of adsorbed aggregates. For the investigations we use a specially developed optical interference enhanced microscopy technique.

2.) *How line tension affects the shape of adsorbed solid aggregates.* High resolution AFM shows that the contact angle of nano-sized sessile droplets (solid aggregates) of C60 decreases with size. This is an indication for a negative line tension.

3.) *How the interfacial properties affect (delay) the coalescence behavior of sessile droplets.* Contrary to intuition sessile droplets of completely miscible liquids do in many cases not fuse instantaneously upon contact. This delay in droplet fusion is caused by surface flow due to interfacial tension gradients.

Details:

Molecules, which form layered structures in their solid phase (long chain alkanes, alcohols, fatty acids, etc.) show an amazing variety of different topologies (droplets, domains, films, layers, terraces …) if they are deposited as molecularly thin films at solid/gas interfaces. These topologies depend on surface coverage, temperature, and preparation history as exemplified in **Fig. 1** with $C_{30}H_{62}$ at SiO_2/air-interfaces:

Above $T > T_{sf}$ (sf = "surface freezing") all alkane is molten. It forms a completely wetting film of uniform thickness.

Below T_{sf} the alkane forms a single solid monolayer adjacent to the solid surface ("surface freezing"). If the overall coverage is not sufficient to form a complete solid monolayer ("submonolayer coverage"), monolayer domains coexist with a submonolayer of individual alkane molecules. The alkane distribution between monolayer domains and submonolayer varies with temperature and reveals details on the interfacial interactions (see **Fig. 1**).

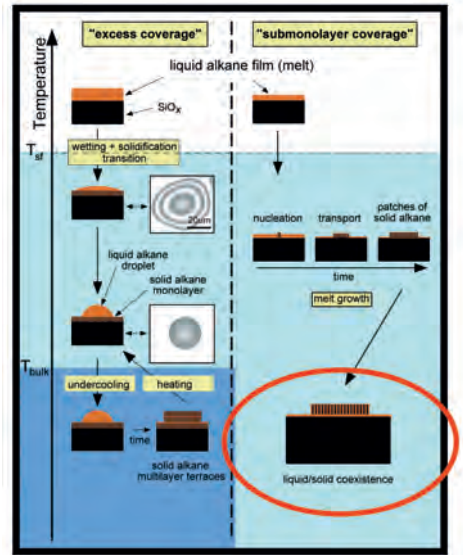
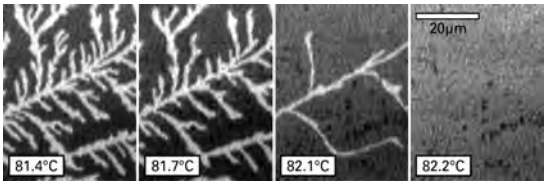


Fig. 1: Various alkane film topologies as a function of coverage and temperature. We find that this phase/topology diagram is generic and valid for many rod-like molecules. Currently our research activities focus on the equilibrium coexistence of monolayer domains and liquid film.

If the alkane coverage exceeds one monolayer ("excess coverage") liquid bulk droplets coexist with the frozen monolayer. Below the bulk melting temperature T_{bulk} these droplets solidify and form multilayers of solid lamellae.



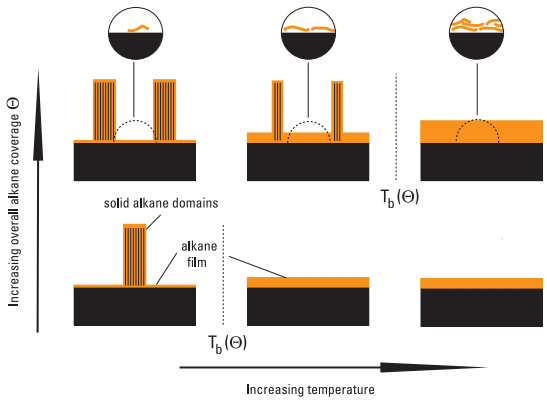


Fig. 2: Partial melting of C40 domains upon temperature increase (top). Schematic of the coexistence of solid domains with a liquid film as function of temperature and overall deposited amount of molecules. This behavior is generic for many molecules (see Fig. 3).

Meanwhile it has been shown that these various phases/ topologies are generic for many rod-like molecules. There are still many open fundamental questions like: Do the wetting and the surface freezing point at T_{sf} coincide? What is the molecular ordering at the interface between the liquid droplet and interface between T_{sf} and T_b? What are the transport properties of the molecules in the submonolayer or above the frozen monolayer?

The temperature dependence of the alkane partitioning between domains and submonolayer film gives new insights into the properties of the submonolayer film (e.g., it behaves like a 2d gas). **Fig. 2** shows a schematic of the partial, gradual melting of C40 domains as the temperature is increased and a sketch revealing the relation between overall surface coverage and temperature of complete melting of the solid domains ($T_b(\Theta)$). This general behavior has now also been observed for long chain alcohols **(Fig. 3)** corroborating the general relevance of the scheme of **Fig. 1**.

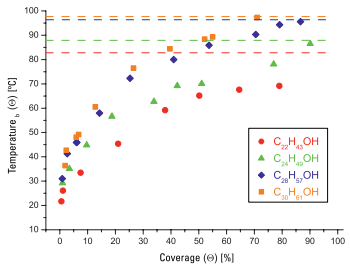


Fig. 3: Temperature of complete melting of long chain alcohol domains ($T_b(\Theta)$, see Fig. 2) as function of the coverage Θ (in % of complete monolayers, dashed lines = melting temperature of a complete monolayer ($T_b(\Theta=1)$).

We also investigate the question of the magnitude and the sign of line tension, which has been under discussion since its first mentioning by Gibbs about a century ago. **Fig. 4** shows that very low coverages of SiO_2/air-interfaces with C60 leads to nano-sized sessile C60 droplets (contact area diameter << 100 nm). With these droplets we could image directly the impact of line tension on the droplet topology. Smaller droplets show a smaller contact angle indicating a negative line tension of about -10e-11 N. The data suggest a crossover from 3-dimensional domains at contact areas below 10 nm radius. This crossover and the existence of such small 2-dimensional domains are currently under investigation. It would give new insights into understanding nucleation.

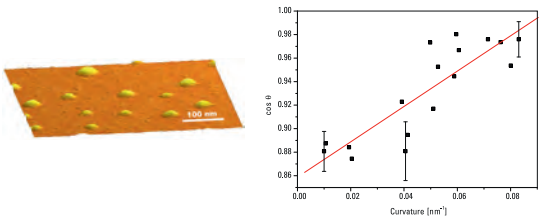


Fig. 4: Nano-sized C60 droplets and their contact angles as function of the curvature (size).

Another project investigates the influence of interfacial interactions on the fusion of (macroscopic) droplets of completely miscible liquids. Quite unexpected, sessile droplets of completely miscible liquids do not fuse instantaneously after contact (both, capillary and volume free energy favor fusion!). Instead, after a first contact, a liquid film/bridge is formed between the droplets **(Fig. 5)** and they repel each other and move over the surface („chasing" droplets). Supposedly this separation is stabilized by flows driven by surface-tension gradient between the two liquids (Marangoni-effect).

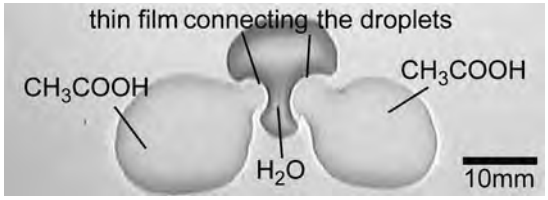


Fig. 5: Delayed fusion between droplets of completely miscible liquids.

Future Plans:

In the future the investigations on the influence of the interface on phase transitions and 2d transport phenomena will be extended to other rod-like substances (fatty acids, short polymers, liquid crystalline materials) as well as other planar substrates (TiO_2, etc.) to work out the more general aspects of the findings.

We will also focus more on the early stages of phase transitions, on molecularly-sized 2d and 3d aggregates and nucleation. Our system is well-suited to specifically investigate the various interfacial influences ("active" interfacial sites) on nucleation and growth). We will investigate the nucleation (growth) of 2d as well as 3d systems. In the latter case we may use the fairly well specified, self-organizing 2d (fractal) domain patterns as templates to investigate the nucleation and growth of 3d systems (a simple example: water condensation on these surfaces).

We will investigate the reasons why the 2d films solidify in certain structures (e.g., fractal 2d domain shapes, terraces, etc.) or what determines the shape of molecularly sized 3d structures (e.g. the influence of line tension on droplet shape). The findings will be used to build optimized structures for organic hetero-junction photovoltaic cells in a collaborative project with academic and industrial partners.

In addition we will investigate the transport properties of 2d systems (the molecular transport in submonolayer films) in an international graduate school with TU Berlin.

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From Molecular Modules to Modular Materials

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Since 2004: Director National Laboratory for Materials Science (NIMS), Tsukuba, Japan.
Since 2008: Professor (University Würzburg)
Chemische Technologie der Materialsynthese

Within the last decades, self-assembly as principle in material science has gained considerable importance and attracted increasing attention in chemistry, physics, and material science. In comparison to traditional material manufacturing self-assembly has potential advantages, such as parallel production, molecular dimension control, defect tolerance, self-repair, and increased life-time. The modularity offers synthetic simplicity and rapid adaption to specific needs. Considering the energies involved self-assembly can be envisioned as key technology in sustainable and environmentally safe fabrication, relying on aqueous media predominantly.

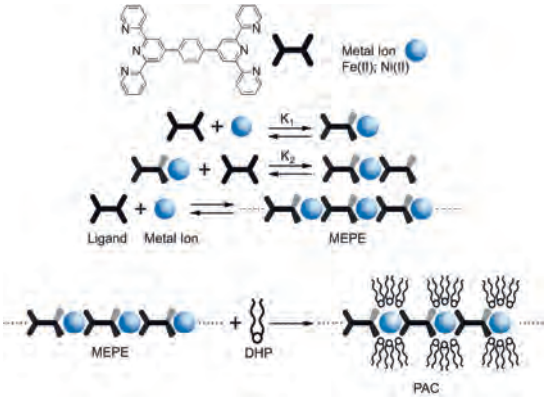
Starting from readily accessible components, self-organization allows tailoring the final material architecture through the judicious design of the building blocks and interactions. The principles of self-assembly are inspired by nature, based on weak and competing interactions, such as hydrogen bonding, metal ion coordination, van der Waals interactions, as well as reversible covalent bonds including esters, disulfides, and cycloadditions. Where biological systems continually demonstrate the delicate control on all levels of the architecture to influence structure and function, material science is still in progress of unraveling the *Aufbau-rules* for self-assembly of hierarchical architectures.

Materials built up through weak interactions exhibit under ambient conditions dynamic behavior, including assembly, disassembly and reconstruction. In addition, these materials can be adaptive and responsive to external triggers, such as temperature, pH, solvent, ionic strength or external fields. These phenomena are unavailable in classical materials based on covalent bonds.

Our interest focuses on the investigation of the underlying principles of self-assembly in complex systems such as metallo-supramolecular coordination polyelectrolytes and architectures based on these polymers.

While the characterization and investigation of kinetically inert transition-metal complexes can be conducted by standard analytical methods, the investigation of dynamic polymeric assemblies formed by kinetically labile transition-metal complexes has remained challenging. 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 **(tpy-ph-tpy)** and kinetically labile transition metal ions including Fe(II), and Ni(II).

The ability to tune the binding affinity by choosing the appropriate metal ion and ligand as well as the well-defined stereochemistry of complexes makes these building blocks promising candidates for the assembly of dynamic and functional metallo-supramolecular coordination polyelectrolytes (MEPEs) **(Scheme 1) [1, 2]**. The synthetically appealing preparation and the readily availability of MEPEs has stimulated research concerning the embedding of MEPEs in mesoporous materials **[3]**, Layer-by-Layer thin films **[2]**, electrochromic **[4]**, and magnetic materials **[5]**.



*Scheme 1: Metal ion-induced self-assembly of Fe(II) or Ni(II)acetate and 1,4-bis(2,2':6',2''-terpyridine-4'-yl) benzene **(tpy-ph-tpy)** leads to positively charged metallo-supramolecular coordination polyelectrolytes (MEPE). The binding constants of terpyridine and first row transition metal ions are large enough to support macroscopic dynamic assemblies. Due the charge MEPE are soluble in aqueous media. The coordination geometry and the design of the ligand result in a rigid-rod type structure. Self-assembly occurs in two steps (middle), the binding of a metal ion and a ligand followed by coordination of a second ligand under formation of the bis-terpyridine complex. Each assembly step is characterized by a binding constant K_1 and K_2. Sequential self-assembly with amphiphiles such as dihexadecyl-phosphate (DHP) results in the corresponding polyelectrolyte-amphiphile complexes (PAC), which can be incorporated into extended architectures such as Langmuir-Blodgett films.*

The molar mass distribution of MEPE depends on the total concentrations, the stoichiometry of the constituents as well as external parameters such as pH, solvent and temperature. In a first approximation, the self-assembly of MEPEs and their dynamic equilibrium of association and dissociation is based on the law of mass action. Following this principle we developed a theory that allows us to describe and predict the molar-mass distribution of MEPE as a function of experimental parameters. The theory predicts an exponential growth of MEPE as a function of concentration if the stoichiometry of ligand and metal ion is one. Notably, the stoichiometry has a strong impact on the average molar mass **(Fig. 1)**.

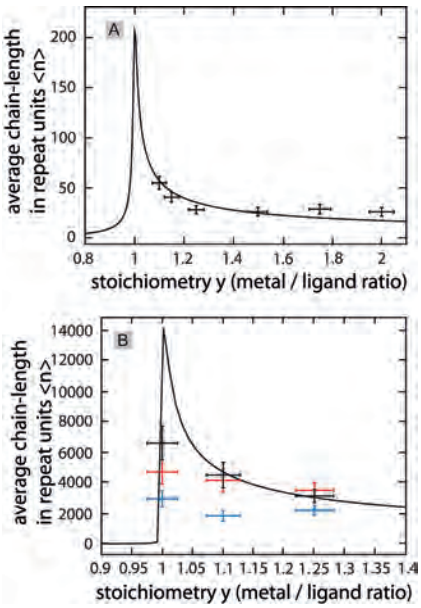


Fig. 1: Average number of monomers per chain <n> as a function of stoichiometry, y, for MEPE assembled from tpy-ph-tpy and Ni(II) (A) and Fe(II) (B), respectively. The concentration was kept constant during the measurement. Symbols resemble AUC measurement, while lines show fitting curves obtained by our theoretical model. The samples were equilibrated for different times: A) one sample equilibrated for 28 days, including fit and error bars, indicated by size of the symbols. B) blue for 1 day, red for 2 days, black for 9 days, a fit could only be obtained for the longest equilibration time; the error of measurement is indicated by the size of the symbols. Here, the stability constants of Fe(II, Ni(II)) and terpyridine are used ($log[K_1] << log[K_2]$).

Starting from ligand excess, the stoichiometry curves (Ni-MEPE **Fig. 1A** and Fe-MEPE **Fig. 1B**) show a steep increase in average molar mass as the stoichiometry, y, approaches one. Apparently, only small assemblies are present in solution in this regime, which self-assemble abruptly when the ligand and metal ion concentrations converge. Above the 1:1 stoichiometry the average molar mass gently decreases and approaches an almost constant value. Notably, even if an excess of metal ions is present in the solution, macromolecular assemblies are formed because K_2 is much larger then K_1 and therefore the equilibrium is on the side of macromolecular species. In contrast, an excess of ligand results in small assemblies presumably mostly dimeric species, consisting of two ligands and a metal ion, which are favorable due to large K_2 value. As a result, we observe a strong asymmetry in the curve of the average molar mass in close proximity to 1:1 stoichiometry. The abrupt change can be envisioned to be used in rheology to open an avenue for the construction of smart materials, e.g. if the stoichiometry is manipulated by an external trigger.

These findings were confirmed by viscosity measurements and molar mass determination using analytical ultracentrifugation. Not surprisingly we also find that MEPE solutions are thixotropic, another property of technological interest.

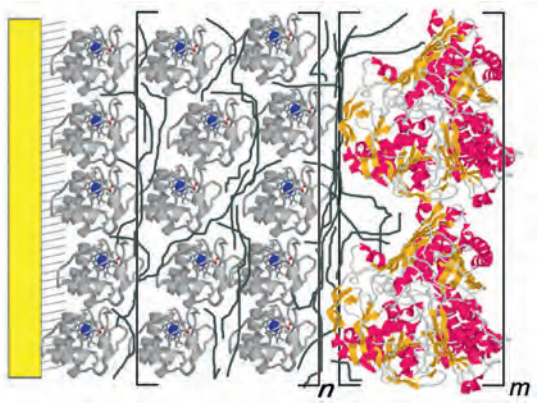


*Fig. 2: Scheme of the two protein multilayer assembly for superoxide (O_2^-) detection. A cytochrome C **(cyt c)** monolayer is formed on MUA/MU (1:3) modified gold electrodes. The cyt c multilayer is built by alternating incubations in PASA and cyt c solutions. Finally, multilayers of PEI/XOD are assembled on the surface.*

Other areas of interest include structure-property relationships in functional materials based on polyoxometalate clusters **[6]** and fullerenes **[7]** as well as the application of self-assembled architectures in bio-molecule mediated sensing **[8, 9]**. We demonstrated that a sensor carrying a thin film built-up by Layer-by-layer technique and composed of cytochrome C, polyaniline sulfonic acid (PASA) in combination with xanthine oxidase is effectively detecting and measuring superoxide in solution **(Fig. 2) [8]**.

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Nanotechnology for Bio-Applications

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The research group of nanotechnology for bio-applications uses the methods of nanotechnology for understanding processes relevant to biology and other fields. The aim is to advance in understanding of fundamental processes and use this knowledge for development of practical applications. One direction is devoted to development of advanced drug delivery vehicles and planar membranes with remote release capabilities for studying intracellular processes in the areas of immunology and protein science. Self-assembly of nanoparticles on both spherical particles and planar surfaces, thermal properties on the nano-scale are also in focus. In addition, novel materials with advanced optical and opto-electronic properties are investigated.

The group's goals are:
- understanding intracellular transport of small peptides;
- development of drug delivery vehicles for studying functions and conformation states of proteins;
- research in the area of nano-manipulations at the polymer-water and polymer-air interfaces;
- thermal properties of polymers and localized permeability control of membranes, films, polymers, etc. at the nanometer scale;
- materials with novel optical and opto-electronic properties.

Intracellular processes provide important information for immuno-response of the system, neurological disorder etc. Studying intracellular processes is hindered by intricacy of non-invasive access to the interior of living cells.

Using polymeric capsules and remote release methods, we have recently introduced remote and non-invasive methods of release of encapsulated materials inside living cells. **Fig. 1** demonstrates that a microcapsule filled with fluorescently labeled molecules is up-taken by a living cell. The walls of the capsule are functionalized with nanoparticles which absorb light energy and convert it to heat. In addition to nanorods, spherical nanoparticle aggregates produce absorption in the "bio-friendly" near-IR (infrared) part of the spectrum. The aggregation of nanoparticles can be induced either by concentration or by shielding the stabilizers on the nanoparticles. Local, nanometer-size, heating by a biologically friendly near-IR laser light affects the permeability of the outer polymeric shell allowing materials to be released remotely. The feasibility of release inside living cells was recently shown. This enables studying various intracellular processes triggered at a desired point in space and time.

The principles of remote release are also looked at for controlling the permeability of membranes.

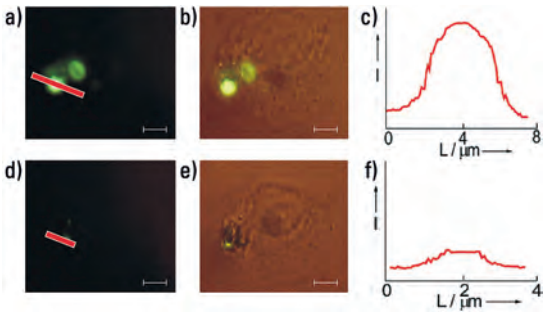

Fig. 1: Sequence of images showing the release of fluorescent AF-488 dextran inside a living MDA-MB-435S cancer cell. a) Fluorescence image of a filled capsule; b) both transmission and fluorescence images of the capsule inside the same cell; c) fluorescence intensity, I, profile plotted along the red line in a). Figure 1 d) - f) present similar data after exposing the cell to a laser beam. The scale bars in all images correspond to 5 µm.

Fig. 2 presents remotely controlled nanometer scale polymeric membranes. The remote action is achieved by exposing the membrane functionalized with absorbing nanoparticles to a laser beam. The nanoparticles locally affect the permeability of polymeric membranes increasing it transiently under the action of the laser beam, and thus allowing molecules to pass through. This "smart" membrane seals itself after laser illumination is switched off. The process is repeatable as the membrane can be re-activated again with another laser exposure. Controllable membranes are expected to find application in various areas from separation chemistry to neurology.

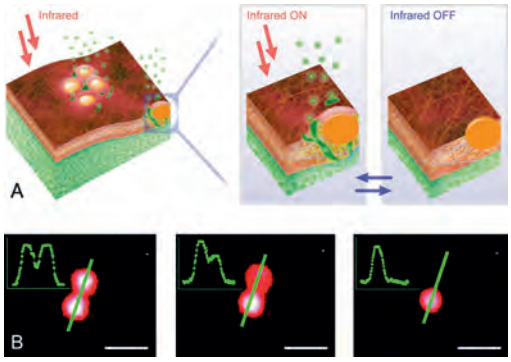

Fig. 2: Remote release from microcapsules. (A) Schematics of nanoparticle functionalized polymeric nanomembranes opening channels upon laser illumination. (B) A polymeric microcapsule shell acts as a reversible nanomembrane. Upon laser light illumination the microcapsule (left image) partially releases encapsulated polymers and reseals (middle). After the second illumination the microcapsule completely releases its content (right). Profiles in the left upper corner are drawn along the green line. Scale bars in all images correspond to 5 µm.

Near-IR absorption can be induced either by nanorods or by aggregates of spherical nanoparticles. In the case of citrate-stabilized nanoparticles, aggregation can be induced by screening charges on the nanoparticles **(Fig. 3)**. On the other hand, the non-aggregated state of nanoparticles can be obtained by direct adsorption at low concentration.

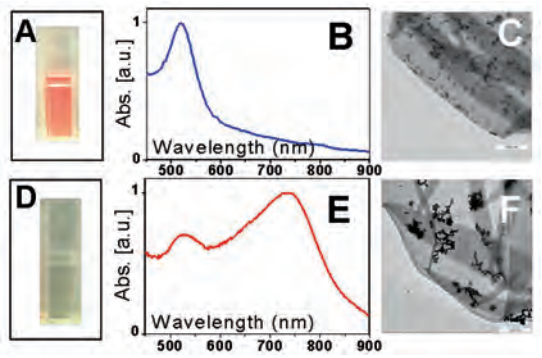

Fig. 3: A solution of citrate-stabilized gold nanoparticles has a red color as seen through a plastic cuvette (A). Its corresponding UV/Visible absorbance spectrum shows a strong absorbance peak at 520 nm (B), TEM image of dry (PDADMAC/Au/PSS)$_4$ shells with non-aggregated gold particles (C). The color of the gold solution after adding salt is blue/gray (D), its corresponding absorption spectrum (E) and the general appearance of these aggregates as seen when inserted in the wall of (PDADMAC/Au/PSS)$_4$ microcapsule (F). Scale bars in TEM images correspond to 500 nm.

The temperature rise on the nanoparticles is the key mechanism that affects the permeability of polymeric membranes. Controlling the distribution of nanoparticles effectively determines the temperature distribution upon laser light illumination. Aggregation of nanoparticles enhances the temperature rise around them; in case of near-IR illumination this effect is enhanced because of increased absorption of nanoparticle aggregates in the near-IR part of the spectrum.

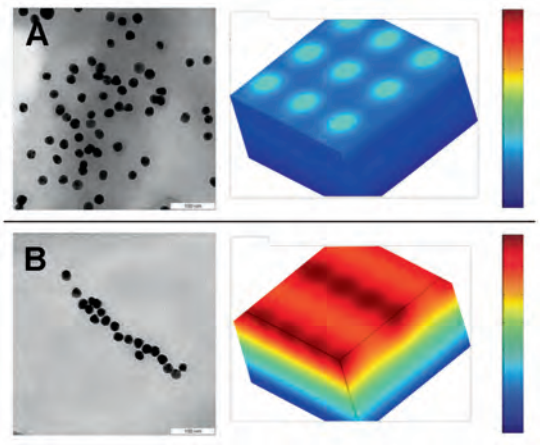

Fig. 4: TEM images (left-hand side) of uniform or non-aggregated (A) and aggregated (B) distribution of nanoparticles. Modelling (right-hand side) of the temperature rise around nanoparticles. Non-aggregated nanoparticles without near-IR laser, (A), are shown together with aggregated nanoparticles illuminated by a near-IR laser, (B). For 20 nm nanoparticles the absorption coefficient at ~ 800 nm is about 0.02, so the temperature rise at 50 mW of incident power of a focussed laser operating at 830 nm is less than 1 degree. For a single line of four aggregated nanoparticles the same conditions lead to the temperature rise of 7 K can (red color). The scale bars in the TEM images are 100 nm.

Future Tasks:

- Investigation of small peptide presentation at the cellular surface relevant to immunology (with Jacobs University Bremen).
- Looking at the functions and structures of proteins inside living cells (with Max-Planck Institute for Biophysical Chemistry, Göttingen).
- Studying thermal properties of ultrathin membranes on the nanoscale.
- Nanoparticle self-assembly at the polymer-water interface for remotely activatable, biocompatible planar thin films/particles and for renewable energy applications.
- Novel materials with optical and opto-electronic properties.

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Active Interfaces and Coatings

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General development of multifunctional coatings, which will possess active and rapid feedback activity in response to changes in local environment, is a key technology for fabrication of future high-tech products and functional surfaces **[1-11]**. These new multifunctional coatings should combine passive components of "classical" coatings and active components, which provide fast response of the coating properties to changes occurring either in the passive matrix of multifunctional coatings (e.g., cracks, local pH change) or in the local environment surrounding the coating (electromagnetic irradiation). The coatings could also have several functionalities.

Nanocontainers

The release properties and re-loading ability of polyelectrolyte-modified halloysite nanotubes, SiO_2 nanoparticles, and polyelectrolyte capsules were studied **[1, 4, 6]**. All nanocontainers revealed an increase of the inhibitor (benzotriazole) release in aqueous solution at alkaline or acidic pH. The application of appropriate nanocontainers depends on the demands required from feedback active anticorrosion coatings. For coatings where the immediate release of the inhibitor is necessary, SiO_2-based or halloysite-based nanocontainers with the shell made of weak polyelectrolytes are preferable. When continuous, gradual release is required, halloysite-based nanocontainers with shell made of one weak polyelectrolyte and one strong or two strong polyelectrolytes are more favourable.

Protective Coatings

Sol-gel films provide excellent adhesion to the substrate and a suitable protection against corrosion by creating a chemically inert barrier between the substrate and the aggressive environment. However, these coatings cannot offer an adequate protection over long term due to the presence of micropores, cracks and areas with low cross-link density. In order to limit the corrosion process, surface modified mesoporous SiO_2 containers loaded with corrosion inhibitor (2-(benzothiazol-2-ylsulfanyl)-succinic acid) were incorporated into the sol-gel films **[2]**. The sol-gel film with containers, which act as a reservoir of corrosion inhibitor, diffuses through the container in aggressive medium and limits the corrosion process.

Halloysite aluminosilicate nanotubes with 15 nm lumen, 50 nm external diameter, and length of 800 ± 300 nm were developed as a container for loading, storage, and controlled release of anticorrosion agents and biocides **[4, 10]**. A fundamental research on nanoassembly to control the release rate within hours, days and months through varying internal fluidic properties and formation of nanoshells in the tube ends is in progress. Sustained activity, food additions, fertilizers, and drug sustained release, plastic fillers, radio wave adsorbing coating with metalized halloysite, and specific ion adsorbent are also in the list of possible halloysite applications. Halloysite nanotubes are available in thousands of tons, and remain sophisticated and novel natural nanomaterials.

Fig. 1: Long term corrosion test: aluminium alloy covered by the polyelectrolyte/inhibitor coating (left) and unmodified aluminium plate (right).

Multicomponent coatings formed by polyelectrolyte multilayers demonstrate a novel method of corrosion protection based on formation and deposition of polyelectrolyte multilayers on aluminium alloy surfaces **[3, 8, 9]**. The multilayer nanonetwork exhibits very high corrosion protection due to the nature and versatility of the polyelectrolyte complex. **Fig. 1** shows pictures of samples coated by the polymer/inhibitor complex (left) and without coating (right). Corrosion defects can be observed after 12 hours of immersion in 0.1 M NaCl on the unmodified aluminum whereas the sample with the polymer/inhibitor complex does not exhibit any visible signs of corrosion attack even after 21 days of immersion. The anticorrosion activity of the polyelectrolyte coating is based on the following mechanisms: 1) pH buffer formed by polybase and polyacid complex suppresses pH changes caused by corrosion degradation; 2) coating regeneration and defect elimination due to relative mobility of polymer chains in swollen state; 3) polyelectrolyte layers form a carrier for the inhibitor allowing its release on demand; 4) polyelectrolyte nanonetwork provides a barrier between surface and environment.

Sonochemistry with Nanoparticles

The collapse of the critical cavitation microbubble in liquids under ultrasonic treatment results in an enormous concentration of energy from the conversion of the surface energy and kinetic energy of the liquid motion into heat or chemical energy. The high local temperatures (5000-7000 K inside a cavitation bubble) and pressures combined with rapid cooling provide unique means for forming nanomaterials with non-equilibrium structure under extreme conditions **[12-19]**. The characteristics of the ultrasonically produced nanomaterials can be changed by decorating it with suitable hydrophilic and hydrophobic organic moieties.

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Sonication of silicon or other water-immiscible oils in a protein or polymer aqueous solution results in the formation of protein containers which have a polymer shell and an oil core **[13, 15, 17, 19]**. Small containers with size less than 3 µm are automatically sedimented after 3 months aging due to the high density of the shells while big containers tend to float on top of the dispersion. To further functionalize the container, magnetic or other nanoparticles can be deposited

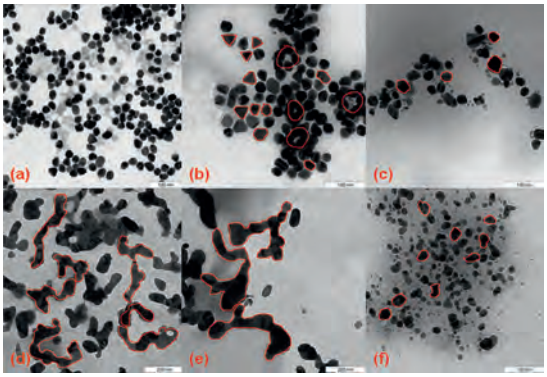

Fig. 2: Transmission electron microscopy images of (a) the control gold nanoparticles; (b) gold-silver nanostructures formed after sonication in aqueous solutions of silver nitrate and sodium borohydride; (c) gold-silver sonication of gold nanoparticles in silver nitrate and poly vinyl pyrrolidone in ethylene, (d) gold-silver after sonication in the presence of silver nitrate and sodium dodecyl sulphate in propanol and (e) in water; (f) gold-silver composites after sonication in the presence of silver nitrate and polyethylene glycol.

on the surface of the prepared containers by using the layer by layer technique. The loading of a dye in the containers shows the feasibility and simplicity used as carrier system. The loaded dye is stably kept inside and safely delivered for several weeks. The size of the containers is influenced by the power distribution in the ultrasonic vessel. An uneven power distribution in the ultrasonic vessel results in a broad size distribution of the prepared microspheres.

Stable monodisperse gold nanoparticles with the average diameter of 30 nm were used for modification by ultrasound at room temperature. The prepared gold nanoparticles were mixed with silver salt and successively sonicated step by step **[12]**. The successive ultrasonic treatment was found as the optimal one because it helps to avoid undesirable aggregation of gold nanoparticles and partly reduces silver ions during the sonication. The type of surfactant influences the size and shape of gold-silver alloys as well as the duration of the ultrasonic treatment adjusts the complete reduction of silver ions on the gold surface. Only 10 minutes of sonication are enough to form monodisperse polygonal gold-silver structures and less than 1 hour for their production with PVP in ethylene glycol solution **(Fig. 2)**. More than 1 hour of ultrasonic irradiation is required to create gold-silver worms or net-like gold-silver nanostructures capped in between with SDS either in water or propanol. This effect was noticed for worm or net-like gold-silver nanocomposites in the presence of SDS either in propanol or in water. XRD and ED patterns of final samples proved the presence of polycrystalline or amorphous gold-silver nanoalloys.

The similar effect of ultrasonic treatment on the crystallinity and activity of platinum nanoparticles was also observed **[14]**. Amorphous platinum nanostructures were formed after 20 min of sonication in water, whereas in poly vinyl pyrrolidone or ethylene glycol solutions they became crystalline. The fastest catalysis was driven by platinum nanoparticles after sonication in ethylene glycol solution for 20 min, while the lowest one was found for those after the ultrasonic treatment for one hour in poly vinyl pyrrolidone aqueous solution.

Multilayered Na^+-montmorillonite clays intercalated with Au nanoparticles were synthesized by direct ultrasonic impregnation of pre-formed gold colloid into the clay matrix. The sonicated composite product consists of Au nanoparticles homogeneously dispersed in the clay. The sample loaded from 4.2 % wt. colloid solution provides the saturation level for Au impregnation into clay material. The nanocomposites are thermally stable as was shown by thermogravimetric analysis. No aggregation of the gold nanoparticles was observed during calcination.

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Ordering of Functional Nanoparticles

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Due to the unique dimension and the size-dependent physicochemical properties derived thereof, organization of colloidal nanoparticles (NPs) not only leads to advanced materials, but also provides experimental accessibility to understand the packing symmetry and the interaction balance of elemental particles. Up to date, however, our capability to instruct colloidal NPs to self-assemble into tailor-designed structures is limited. To overcome this limit, one should re-visit the thermodynamics associated with self-assembly of colloidal NPs, such as the acting nature of various forces exerted on the NPs and the balance between the forces. In parallel, one should also enhance the capability to synthesize colloidal NPs with anisotropic morphologies and/or patterned surface functionality. To achieve a better control of the spatial configurations of the self-assemblies of colloidal NPs and even a flexibility to tune their spatial configurations by using external fields or stimuli, new flexible templates are also highly demanded such as the interfaces between two immiscible fluids and molecular self-assemblies. Only after accomplishing the above three tasks, one will be able to direct self-assembly of colloidal NPs in a spatially and temporally programmed fashion, leading to Supraparticles with the structural and functional complexity embodied in supramolecules **[1]**.

A. Interfacial Behavior of Nanoparticles

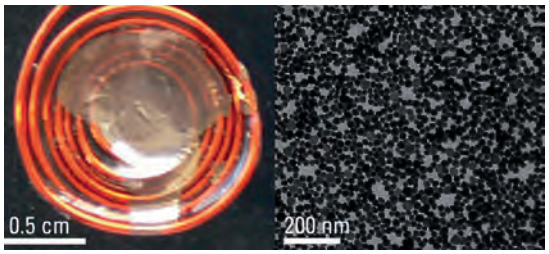

Fig. 1: Optical photograph (left) and transmission electron micrograph (right) of the dried freestanding monolayer film of 12 nm gold NPs, obtained by their self-assembly at the water/pentanol interface in a Petri dish, followed by heating at 48 °C for 3 h.

The interfaces between two different phases allow molecules and macromolecules to accumulate and cross, which are of essential importance in everyday processes from biology such as transmembrane diffusion to geology such as oil extraction. Despite of a long research history in colloid science, the interface has just recently been appreciated by other research disciplines; the fluidic character allows formation of the NP monolayer films over large areas (at least several cm^2). Taking the advantage of the exceedingly high surface energy of bare NPs, we succeeded in using water/oil interfaces to create dried freestanding monolayer films of metallic NPs, such as gold, silver, and platinum, with thickness ranging from 5 to 25 nm. **(Fig. 1) [2]**. It is of interest that the resulting freestanding films showed a certain mechanical robustness; the Young's modulus of dried freestanding films of 12 nm gold NP monolayers was determined as 1.6 GPa.

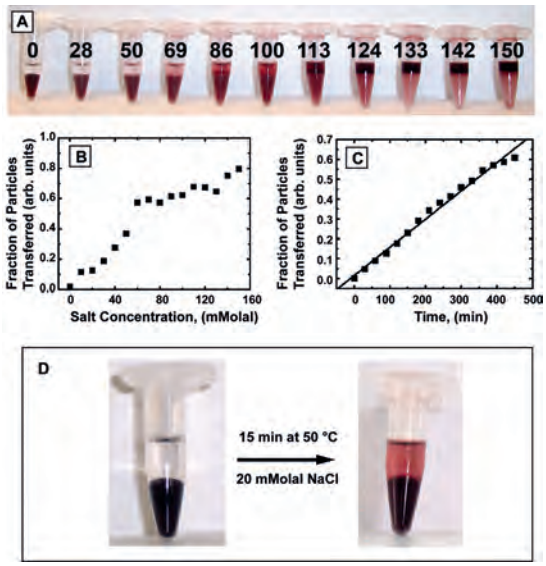

Fig.2: Poly (OEGMA-co-MEO_2MA) capped gold NPs spontaneously transfer across the salty water-toluene interface.
A) Optical image of poly (OEGMA-co-MEO_2MA) capped gold NPs originally dispersed in aqueous NaCl solutions, two days after creating a biphasic system with toluene. The NaCl concentrations, in mM, are shown on each vial.
B) The fraction of Poly (MEO_2MA) capped gold NPs transferred across the salty water-toluene interface after 1 h as a function of salt concentration.
C) The fraction of poly (MEO_2MA) capped gold NPs transferred across the salty water (150 mM NaCl) - toluene interface as a function of time.
D)Optical image of Poly (OEGMA-co-MEO_2MA) capped gold NPs originally dispersed in a 30 mM NaCl solution in water 15 min after the introduction of toluene at room temperature and 15 min after heating the biphasic mixture at 40 °C.

In order to use the interface well to template self-assembly of colloidal NPs, our research focus was also laid on mimicking the interfacial behavior of molecules. With the aid of atom transfer radical polymerization, we synthesized various polymers with one end terminated with different functional groups such as disulfide, carboxylic acid and catechol groups to be grafted on different NPs. When NPs were coated with stimuli-responsive polymer brushes, their surface energy, mainly hydrophobicity here, were able to be tuned in response to the environmental stimuli such as ionic strength and temperature. The stimuli-responsive hydrophilic-hydrophobic transition allowed NP transfer between the aqueous and organic phase across the interface when they were brought into a water/oil biphasic system **(Fig. 2) [3]**. As well known, colloidal NPs quickly attach to the interface, which should block the NP transfer across the interface. Accordingly, this new trans-interfacial behavior of NPs is size-dependent.

B. Directed Self-Assembly of Nanoparticles

One of our major research activities associated with directing self-assembly of colloidal NPs is to understand the nature of various forces exerted on NPs during the self-assembly and

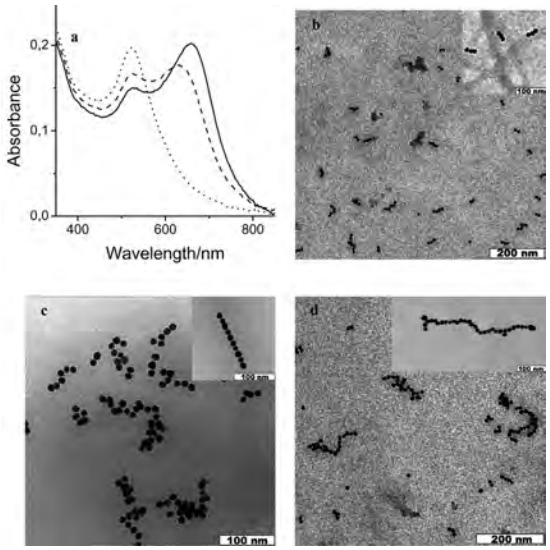

Fig. 3: (a) UV-vis spectral evolution of gold NP dispersions as a function of the water-to-acetonitrile volume ratio, 1:1 (dotted curve), 1:2 (dashed curve), and 1:3 (solid curve). TEM images of chains of gold NPs obtained using water-to-acetonitrile volume ratios, 1:1 (b), 1:2 (c), and 1:3 (d). The corresponding high magnification TEM images are shown in the insets.

how to control the thermodynamic balance of the forces between the NPs. It is well recognized that charged NPs are not stable and tend to aggregate upon adding salt into their dispersions due to the dramatic reduction of the electrostatic repulsion. After capping negatively charged gold NPs with thiol-ligands to enhance the dipolar interactions arising from the uneven surface morphology and non-uniform surface crystalline facets by Au-S bonding, we recently found that the gold NPs commenced to chain up and the chain growth could be tuned exclusively by the electrostatic repulsion between the NPs **(Fig. 3) [4]**. Lowering the electrostatic repulsion between the gold NP led to longer the NP chains. As compared with the ionic strength of the surrounding media, the dielectric constant provided a better tool to tune the electrostatic repulsion between the charged gold NPs. Our study suggests that although the long-range electrostatic repulsion between charged particles is isotropic in nature, it can act in an anisotropic way in the presence of short-range anisotropic interactions such as dipolar interaction, thus endorsing an anisotropic agglomeration of NPs. This allows us not only to direct self-assembly of colloidal NPs in a controlled one dimensional way but to gain a better understanding of nucleation and agglomeration of charged species in aqueous media where electrostatic forces are not negligible.

C. Colloidal Lithography

Self-assembly of colloidal NPs should be integrated with macroscopic and microscopic devices in order to make a great impact on our society. The patterning techniques used to construct devices are mainly based on lithography, which are little accessible to chemists, biologists and materials scientists. Accordingly, in the past years our journey of using single and double layers of hexagonally closely-packed colloidal microsphere continued to pursue a cheap, flexible, and nanochemcial way to create patterns with feature complexity comparable to those obtained by lithography. Recently, we have successfully developed a stepwise angle-resolved colloidal lithography with the aid of plasma etching of the colloidal template.

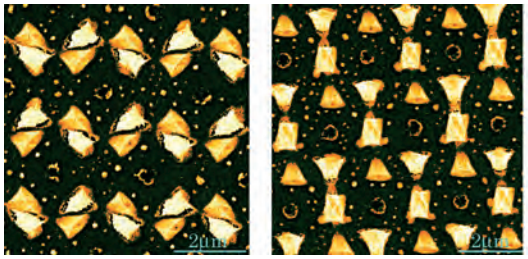

Fig.4: Heterogeneous binary arrays of gold (yellow) and silver (white) NPs obtained by stepwise angle resolved colloidal lithography.

With the new technique, we were able to create 2D and even quasi-3D patterns on planar substrates with defined but varied lateral and vertical heterogeneity, some of which are hard to create even by lithography **(Fig. 4) [5]**.

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Molecular Assemblies of Biomimetic Systems and Nanostructured Design

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Biomimetics has proved very useful in the design and fabrication of new functionally structured materials on the micro- and nanoscale. Biomimetics refers to human-made processes, devices, or systems that mimic or imitate certain aspects of biological systems, which has proven useful in providing biological inspiration from natural efficient designs. However, biomimetic is not limited to just copying nature because, with the development of modern biology, scientists can directly utilize biological units themselves to construct hybrid nanostructured materials. Thus, some of the manufacturing difficulties of biomimetics can be avoided. Accordingly, the objective of our group is to integrate natural molecular machines such as motor proteins into the engineering of active biomimetic systems so that new functional hybrid nanomaterials can be constructed.

A. Active Biomimetic Systems

Regeneration of ATP Biosynthesis in Assembled Capsules

The F_0F_1-ATPase is responsible for the catalytic synthesis of ATP molecules in biological organisms. They are widely present in the membranes of mitochondria, chloroplasts and prokaryotic cells, where they convert transmembrane electrochemical proton gradients into ADP~P bonds (i.e. ATP). The F_0F_1-ATPase is a well-known rotary motor and probably the best-understood biological molecular motor. ATPase assembled in lipid-modified polyelectrolyte microcapsules is able to perform the process of ATP biosynthesis and provides a novel routine to fabricate bionanodevices. This assembled complex can not only help us to understand the biological function of ATPase molecules but also to construct such an artificial designed system containing ATPase providing a well-defined container for the storage of the energy currency ATP. When vital activities need energy, ATP will be released across the wall of the capsules as power supply **(Fig. 1)**.

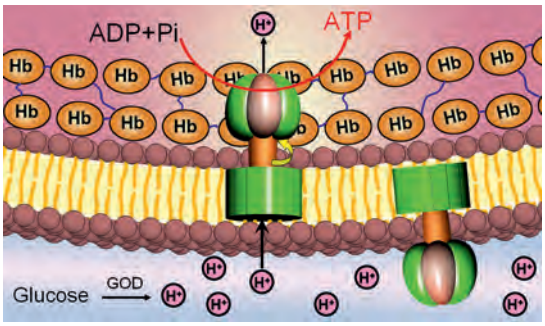

Fig. 1: Schematic representation of the arrangement of CF_0F_1-ATPase in lipid-coated microcapsules.

Assembled Capsule Transportation Driven by Motor Proteins

The linear molecular motor, kinesin, transports chemical payloads along microtubules in the cell. The used filament, microtubule, is polar and has two functions: provide rails or tracks for the kinesin motors and limit the movement in a certain direction. Our group currently focuses on the design and assembly of active biomimetic systems which involve the surface modification of microcapsules with well defined properties, purification of microtubules to link the biomolecular motors, stepping motor proteins, kinesin and the completed assembly of the system. We try to provide experimental evidence on the way the molecular motors generate pulling forces to direct the hollow capsule transportation along the microtubules and further understand the force generation mechanisms. The final system aims at a specific function of hollow capsules as a useful "cargo" for drug delivery in a living matrix by making use of molecular motors **(Fig. 2)**.

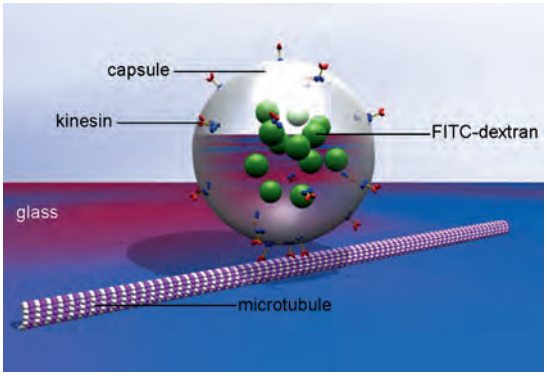

Fig. 2: Layer-by-layer assembled microcapsule as cargo driven by kinesins along a microtubule.

B. Bioinspired Nanostructures

Peptide Self-Assembly

Cationic dipeptides can self-assemble into the structure of vesicles spontaneously under a certain condition. Such a conversion could readily transport genes, into cells through the membrane. Interestingly, these cationic dipeptides can self-assemble into various types of fibrils, strands and tapes in organic solvents via weak intermolecular interactions. The self-assembly behavior of dipeptide nanostructures, 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. Currently, we are interested in investigating the conversion process quantitatively and building up models. We also report that a single dipeptide molecule, which is probably one of the smallest peptide gelators, can self-assemble into persistent length nanofibrils in organic solvents and intertwist further to form gels. Such gels can be readily used to encapsulate quantum dots and gold nanoparticles through gelating the organic solution of nanocrystals. These organic-inorganic complexes can find their applications as optical and electronic materials and devices **(Fig. 3)**.

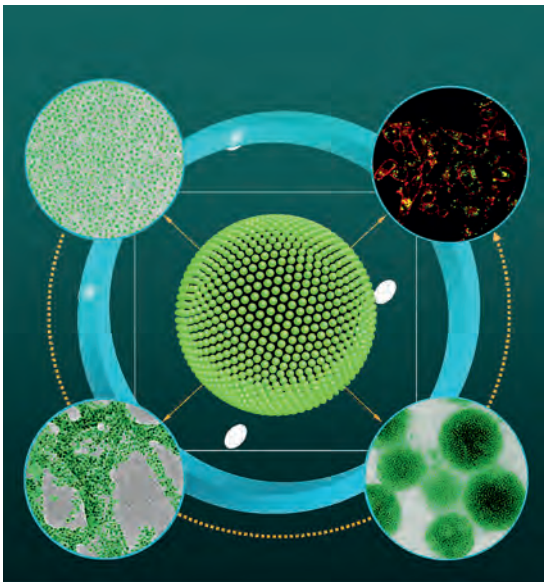

Fig. 3: Biocompatible water-dispersible 3D colloidal spheres can be prepared via the combination of functional lipophilic nanocrystals and a self-assembling cationic dipeptide building block.

Biointerfacing Multilayer Nanostructures

Polyelectrolyte multilayer-supported liposomes or lipid bilayer-coated polyelectrolyte multilayer nanostructures could be fabricated through the conversion of liposomes into lipid bilayers to cover the multilayers' surface in analogy to the cell membrane. These lipid-modified polymer microcapsules should be an ideally supported biomimetic membrane system to mimic a real cell membrane. Polyelectrolyte multilayer-supported lipid bilayer systems should be useful for the understanding of the principles of the interaction of membranes with biopolymers such as proteins, opening the possibility for the design and application of new biomimetic structured materials **(Fig. 4).**

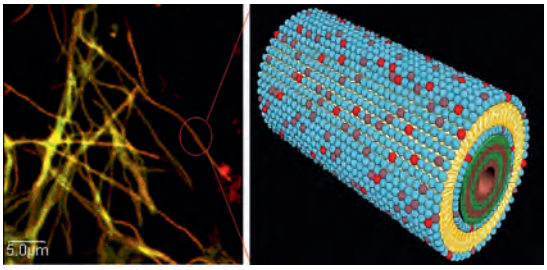

Fig. 4: Schematics of lipid bilayer coating on layer-by-layer assembled luminescent nanotube by liposome fusion.

Biomimetic Capsule as Photosensitive Drug

Photodynamic therapy (PDT) is a rapidly growing methodology to treat cancers, viruses and some special vascular diseases that are accessible to irradiation by visible light. Although light-sensitive drugs or photosensitizers can be activated by light, they should not interact directly with cells and tissue. Light-activated PDT drugs can generate singlet oxygen ($^1O_2$) which is a cytotoxic species to induce cell death. Obviously, this method has good selectivity because the cytotoxic reactions only occur in those tissues exposed to the photosensitizer and light. Hypocrellins and natural perylenequinoid pigments are thought of as potential photosensitizes in PDT.

Hypocrellin B (HB) has a wide absorption band in the visible region and extremely high singlet oxygen ($^1O_2$) generation ability and thus has been receiving intensive interest in PDT. However, HB is insoluble in water which limits its application in clinical treatments. We therefore introduce assembled hollow shells loaded with HB into PDT to overcome the obstacles of hydrophobicity of HB. These hollow shells are meant to deliver drugs into cell compartments and to allow the direct visualization of intracellular drug distribution **(Fig. 5)**.

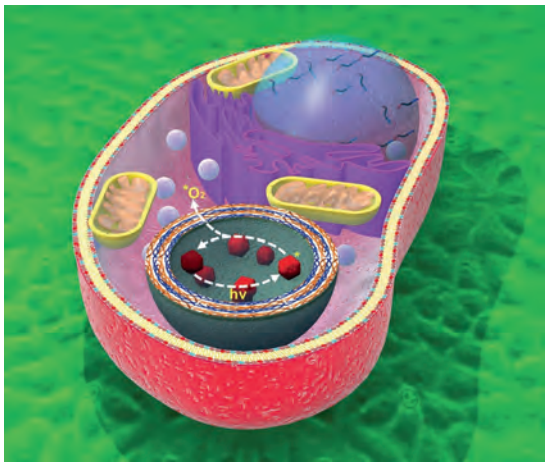

Fig. 5: Photosensitive drugs encapsulated by biomimetic microcapsules to incapacitate cancer cells.

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Supramolecular Materializations

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An important challenge in nanoscience is to fabricate dimension-controllable nano/microscopic organic architectures which exploit the advantageous intrinsic properties and the weak intermolecular forces of their molecular building blocks. Nano/microscopic structure formation from typical (hydrophilic/hydrophobic) amphiphiles such as surfactants and lipids is well matured, and the formation mechanism is well understood. Our interests of research are focused to supramolecular architectures in nano/microscopic and bulk scales from functional components whose structures are far from conventional amphiphiles, which have more possibilities to create versatile assembled architectures and functions. A delicate balance of the intermolecular interactions, such as van der Waals, π-π, hydrogen-bonding, leads to a wide variety of supramolecular morphology and this understanding of hierarchically assembled systems should inspire further studies for supramolecular chemistry, biomimetic structures, nanotechnology as well as their materializations.

The Supramolecular method utilized in our group is controlling the architecture and dimensionality of hierarchical fullerene superstructures by varying the nature of the solvent system. To achieve the hierarchical fullerene assemblies, we have synthesized a series of new type of amphiphilic (solvophilic) fullerene derivatives bearing long aliphatic chains, especially three hexadecyloxy chains (1), and explored them by using the two different intermolecular forces, π-π (C_{60}) and van der Waals (aliphatic chains) interactions **[1, 2]**. By varying the solvent system, the derivative self-organized into vesicles, fibers, cones, micro-spheres, maracas-like, windmill-like sheets, jellyfish-like, left-handed and right-handed spiral objects **(Fig. 1)**. The finding suggests possible synthetic methodologies towards novel dimension-controllable carbon materials.

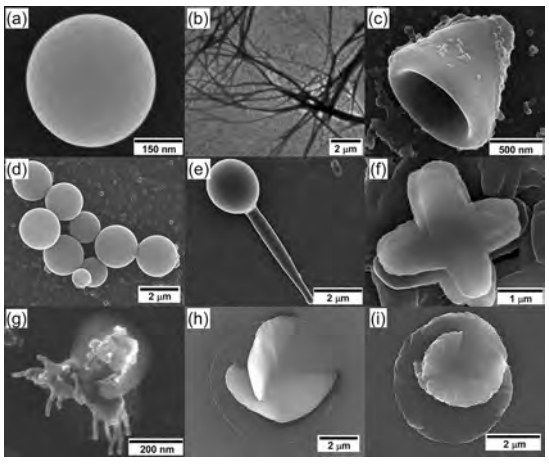

Fig. 1: SEM images of vesicles (a), fibrous (b), conical (c), micro-spherical (d), maracas-like (e), windmill-like sheets (f), jellyfish-like (g), left-handed (h) and right-handed (i) spiral objects of 1 obtained from various solvent conditions.

To further diversify the library of self-organized fullerene superstructures, for instance, with fractal shape, the understanding of the formation mechanism of self-organized microscopic superstructures becomes more important. Hierarchical supramolecular assemblies of micrometer-sized flower-shaped objects **(Fig. 2)** are constructed by transformation of an interdigitated bilayer precursor composed of a fullerene derivative (1). Intermediate transforming structures, which include flat bilayer disks, rolled up and crumpled disks, provide evidence for the formation mechanism of the flower-shaped objects **[1]**.

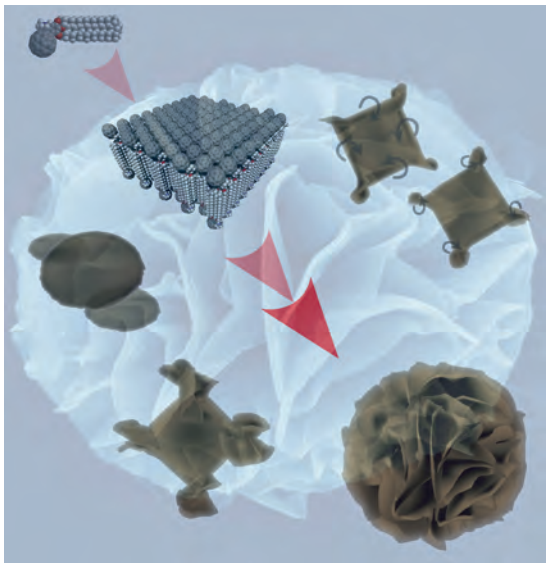

Fig. 2: Formation mechanism of flower-shaped supramolecular assemblies of 1.

A fullerene derivative bearing three eicosyloxy chains (2) self-assembled into micrometer-sized particles with wrinkled flake-like outer surface morphology. The assembled objects have more potential to be useful supramolecular materials due to their quantitative yields from the derivative, well-analyzed nano-assembled architectures (self-organized bilayer), and their ease of hierarchical fabrication on substrates. Thin films of these particles have a fractal surface reminiscent of the Lotus Leaf and feature water-repellent superhydrophobicity with a water contact angle of "152°" **(Fig. 3) [3]**.

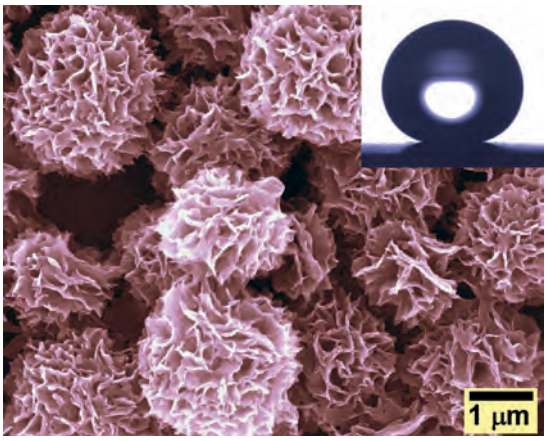

Fig. 3: SEM image of globular assemblies of 2 having nanoflaked outer surfaces. Inset shows a photograph of water droplet on the surface (contact angle of 152°).

A sustainable method for the fabrication of metallic surfaces with rose flower-like fractal morphology was developed by using the supramolecular microparticles of 2 as templates, which possess a nanoflake structure at the outer surface **(Fig. 4)**. Modifying Au nanoflakes with self-assembled thiol monolayers or polymers allows the surface wettability to be adjusted between superhydrophilic and superhydrophobic. Furthermore, Au nanoflakes present excellent substrates for surface-enhanced Raman spectroscopy. The enhancement factor is around 10^5 **[4]**.

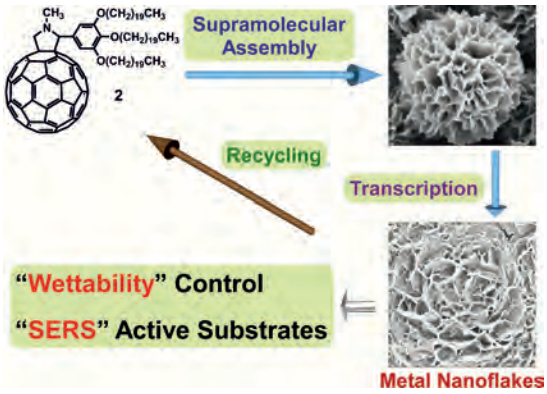

Fig. 4: Schematic illustration for the fabrication of metal nanoflake surfaces via supramolecular assemblies of a fullerene derivative (2) as template objects.

The fullerene derivatives satisfy the requirements for high carrier mobility in the C_{60}-containing mesomorphic materials: a high C_{60} content up to 50 % and a highly ordered mesophase. Thermotropic mesophase of 2 is seen in the temperature range between 62 to 193 °C, and shows optical texture under a polarized optical microscope **(Fig. 5a)**, which exhibits birefringence and confirms the fluid nature. Higher-order peaks, up to (0 0 14), in the XRD pattern reveal a long-range ordered lamellar mesophase comparable to ordered smectic phases **(Fig. 5b)**. The mesomorphic fullerenes feature reversible redox activity and comparably high electron carrier mobility, ~3 × 10^{-3} cm^2/Vs at 120 °C, making them attractive components for fullerene-based soft materials **[5]**.

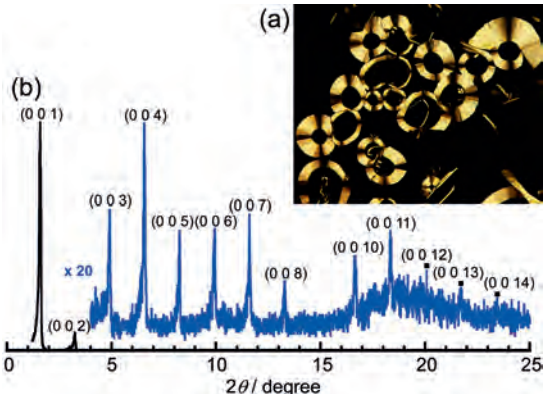

Fig. 5: Polarized optical micrographic texture (a) of mesophase of 2 at 190 °C and the XRD patterns (b) indicating its long-range ordered lamellar organization.

Other areas of interest include supramolecular materials of dipyrrole-diketon type versatile assemblies **[6]**, anion sensible organogels **[7]** and diversification of barbituric acid merocyanine dye architectures by hydrogen-bonding **[8]**.

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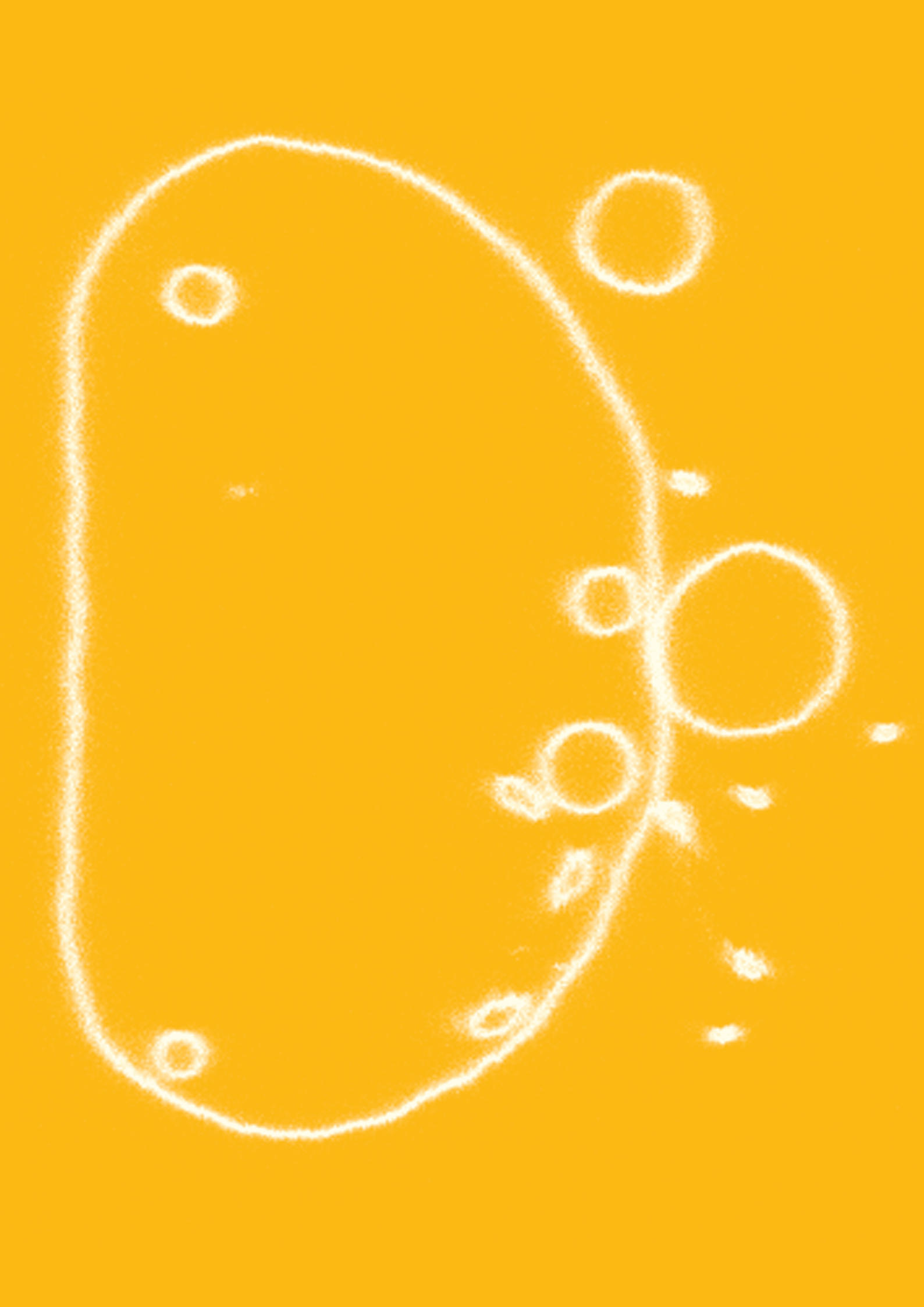


→ Polymers and Proteins
→ Molecular Motors
→ Membranes and Vesicles
→ Networks in Bio-Systems

THEORY & BIO-SYSTEMS

Research in the Department of Theory & Bio-Systems

There's plenty of room at the bottom
Richard Feynman

The researchers and graduate students of the Department of Theory and Bio-Systems form one experimental and several 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; until 2007);
- *Jan Kierfeld* (theory, polymers and filaments; until 2007);
- *Volker Knecht* (theory; proteins and membranes).
- *Christian Seidel* (theory, polymers and poly-electrolytes);
- *Thomas Weikl* (theory, proteins and membranes).

The Theory and Bio-Systems Department is responsible for the International Max Planck Research School on 'Biomimetic Systems'. Until the end of 2008, the department also coordinated the European Early Stage Training Network about the same topic and the European Research Network on `Active Biomimetic Systems'. The graduate programs are managed by *Angelo Valleriani*.

In the following three subsections, the research within the Theory and Bio-Systems Department is described in terms of the underlying molecular systems, the cooperative 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 of cargo particles by several such motors. When these motors belong to two different species, they perform a stochastic tug-of-war as shown in **Fig. 1**.

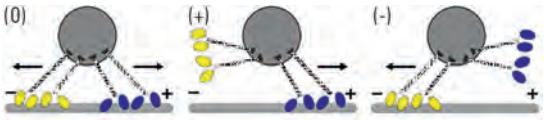


Fig. 1: Tug-of-war between 2 plus (blue) and 2 minus (yellow) motors pulling on the same cargo particle (gray). For configuration (0), the motors block each other so that the cargo does not move. For configuration (+) and (-), the cargo exhibits fast plus and minus motion, respectively.

One particularly intriguing aspect of filaments is the coupling of filament growth to active processes. One example is provided by actin polymerization coupled to ATP hydrolysis. In order to elucidate this process, we introduced a new theoretical model for cooperative ATP cleavage and Pi release as shown in **Fig. 2**.

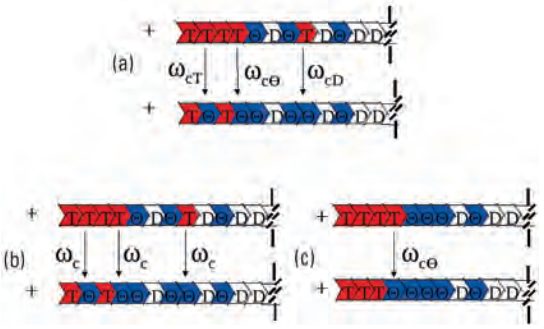


Fig. 2: Actin filaments consisting of three different types of protomers denoted T, Θ and D: (a) Cooperative ATP cleavage depending on the local neighborhood of the T protomer within the filament; (b) Random ATP cleavage and (c) Vectorial ATP cleavage.

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 multicomponent membranes to solid substrates as shown in **Fig. 3.** In addition, the deformation of lipid vesicles by alternating electric fields has been studied experimentally as a function of ion conductivities and field frequency, see **Fig. 4**.

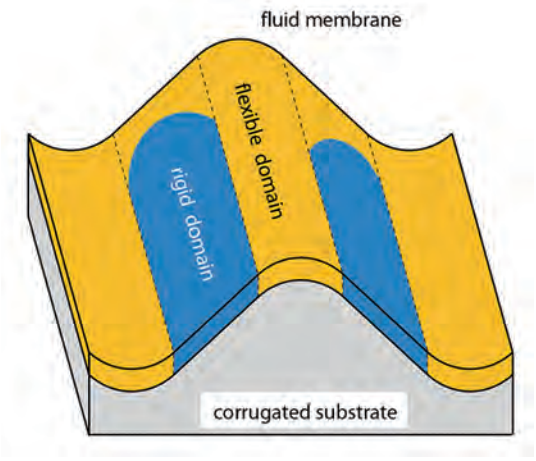


Fig. 3: Fluid membrane on a corrugated, solid substrate with two types of domains (blue and yellow) that differ in their bending rigidity. The blue domains are more rigid than the yellow one and tend to avoid the curved membrane parts provided the line tension of the domain boundaries is sufficiently small.

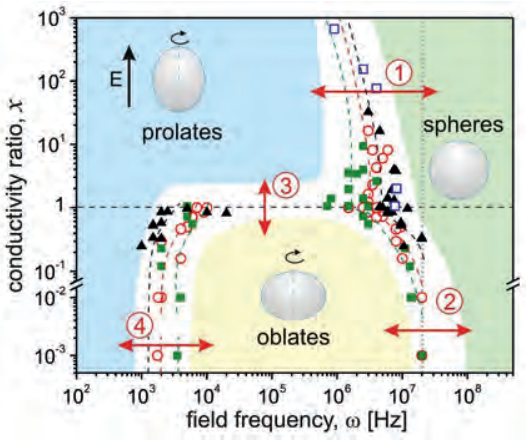


Fig. 4: Morphological diagram for lipid vesicles in alternating electric fields as function of field frequency and conductivity ratio.

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 simple neural networks.

Most of the 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.

The theory of 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. In general, the challenge is to find a theoretical representation that depends only on experimentally accessible parameters.

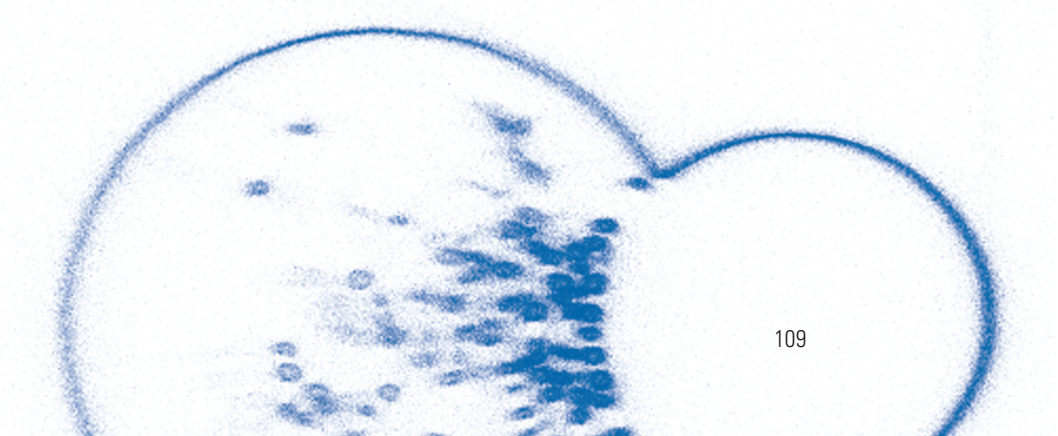
The theoretical models are then studied using the analytical tools of theoretical physics and a variety of numerical algorithms. The analytical tools include dimensional analysis, scaling arguments, molecular field or self-consistent theories, perturbation theories, and field-theoretic methods such as renormalization. The numerical methods include the application of mathematical software packages for calculus and algebra 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, Brownian Dynamics, and Monte Carlo methods. Molecular Dynamics is used for particle based models of supramolecular assemblies; Dissipative Particle Dynamics is useful in order to extend the Molecular Dynamics studies towards larger systems and longer time scales; Brownian Dynamics and 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.

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 departments of the MPI.

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

Reinhard Lipowsky
Director of the Department
of Theory & Bio-Systems



Polypeptides: Amyloid Formers and Molecular Motors

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Proteins and polypeptides in general are biopolymers composed of amino acid residues that fold into well-defined structures depending on their amino acid sequence. Folding is crucial for the function of a protein whereas misfolding can cause severe diseases. Our aim is to understand protein function and diseases on the molecular level. The information on the molecular dynamics of polypeptides accessible experimentally is very limited. Therefore we use molecular dynamics computer simulation techniques to model the process by which proteins sample conformational space. Molecular dynamics simulations which are based on iteratively solving Newton's equations of motion to propagate a system in time and semi-empirical force fields to describe interatomic interactions can provide highly detailed information about the properties of proteins in solution or at interfaces. Here, the protein and its solvent environment are described in atomic detail. Currently, we focus on the molecular basis of so-called amyloid diseases and the function of molecular motors.

Amyloid Peptides

Amyloid diseases including Alzheimer's, Creutzfeld-Jakob disease and bovine spongiform encephalopathy (BSE) are associated with the conversion of a protein from a soluble (functional) form into higher order fibrillar aggregates rich in β-structure. The development of specific agents against amyloid diseases requires an understanding of the (mis)folding and aggregation of fibrillogenic proteins on a microscopic level. In collaboration with Gerald Brezesinski's group from the Interfaces department, we study the folding and aggregation of small amyloid peptides in solution, see **Fig. 1**, and at interfaces, see **Fig. 2 [1-4]**. The systems investigated include model peptides containing between 12 and 18 residues, see **Fig. 1(a,b)**, as well as an 11-residue fragment of the amyloid β (Aβ) peptide associated with Alzheimer's disease, Aβ(25-35), see **Fig. 1c**.

Fibrillogenic peptides, typically, are found to form β-hairpin as in **Figs. 1(a,b)** and **2(a)** or coil conformations. As shown in **Fig. 1(b)** (middle), a predominant conformation has been identified for the inner residues of the model amyloid peptide LSFD **[4]**. Knowledge of a predominant conformation may facilitate the design of possible inhibitors of LSFD aggregation as a testing ground for future computational therapeutic approaches against amyloid diseases. In ordered aggregates, β-hairpins are either placed side by side, see **Fig. 1(a)**, or dissolved often leading to extended conformations, see **Figs. 1(c)** and **2(b)**. Some of these dimer conformations might reflect the structure of fibrillar aggregates, see **Fig. 1(a,c)**.

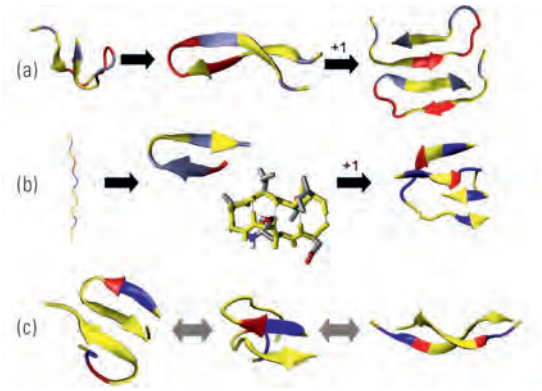

Fig. 1: β-hairpin folding and dimerization of fibrillogenic peptides in solution in molecular dynamics simulations. The model amyloid peptides (a) B18 [1-3] and (b) LSFD [4] as well as (c) the peptide Aβ(25-35) associated with Alzheimer's disease are depicted. Initial and typical backbone configurations during the simulations are shown in ribbon representation. Colors distinguish between hydrophobic (yellow), hydrophilic but neutral (blue), and charged residues (red). In (b), the conformation of the monomer in the folded state is shown as sticks.

For the first time, we have studied reversible β-hairpin peptide folding at an interface, see **Fig. 2(a) [4]**, the formation of side-by-side-hairpin β-sheet dimers **[3]**, see **Fig. 1(a)**, and the conformational distribution of a peptide containing more than ten amino acid residues in dimeric form at equilibrium, see **Fig. 1(c)**, using an explicit solvent model.

The studies are challenging because of the large computational expense of the simulations and the roughness of the free energy landscape underlying folding. Therefore, our initial studies have been restricted to relatively short model peptides. But, using novel methods to enhance the sampling including the coupling of simulations of various copies of the system at different temperatures (replica exchange), we are now investigating larger peptides such the 26-residue peptide Aβ(10-35) in mono- and dimeric form. A non-amyloidogenic peptide of the same size, the (antimicrobial) peptide NK-2, is investigated for comparison.

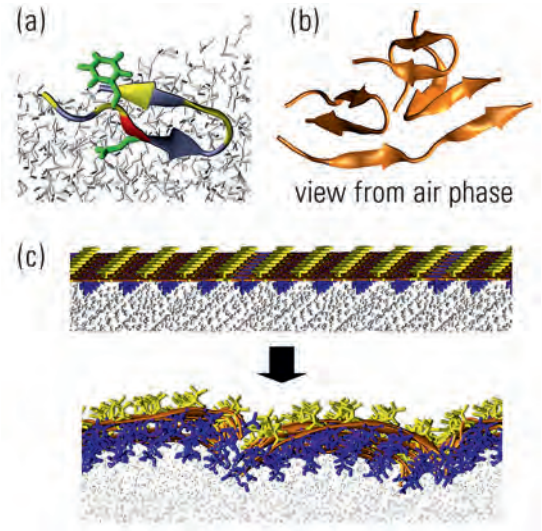

Fig. 2: β-sheet forming peptides at water/vapor interface. An LSFD (a) monomer [4] and (b) tetramer, as well as (c) a crystalline monolayer of the peptide G(VT)$_5$ are depicted. The backbone of the peptides is shown in ribbon representation. In (a), the color code for the peptide backbone is similar to that chosen in Fig. 1, and selected side chains are shown as green sticks. In (c), the side chains of the peptides are displayed as sticks, colors distinguish between valine (yellow) and threonine (blue). In (a) and (c), water molecules are depicted as white sticks.

The synthetic peptide with sequence G(VT)$_5$ synthesized in Hans Börner's lab in the Colloids department has been studied at a water/vapor interface where it forms β-rich crystalline monolayers. Based on data from x-ray scattering and infrared spectroscopy, we modeled an idealized monolayer in which the peptides are extended and form in-register β-sheets over their whole length, see **Fig. 2(c)**, top, and used simulations to refine the structure. We found that the β-strands are strongly bent and that β-sheets are dissolved at the termini as in **Fig. 2(c)**, bottom. When the subphase contains NaCl, both types of ions are strongly adsorbed at the termini of the peptides.

Molecular Motors

The Kinesin molecules represent a large motor-protein family that transports cargoes within a cell by moving on microtubule filaments consisting of α- and β-tubulin dimers coupled to ATP hydrolysis, see **Fig. 3**. Conventional kinesin, henceforth denoted as kinesin, is a homodimer containing two heads by which kinesin binds ATP and walks along microtubules. The molecular details of this process are poorly understood. In order to quantify the energy levels of kinesin in all its nucleotide-binding states, we aim to determine equilibrium constants and activity scales for ATP hydrolysis from quantum-mechanical calculations using a continuum model for the solvent. Test studies to evaluate the accuracy and computational expense of different levels of theory are in progress.

In order to understand the mechanical response of kinesin to the chemical transitions, we are studying the conformational changes of a kinesin monomer in solution and at tubulin during the catalytic cycle using classical molecular dynamics simulations. Structural models based on x-ray crystallography or cryo-electron microscopy are used as input for the simulations. The timescales for each nucleotide state employed here exceed those used in previous studies of the same system by almost two orders of magnitude. We found that the region connecting the head and the adjacent neck region, the neck linker, is highly flexible and, thus, provides a hinge, for all nucleotide states. Currently, we are investigating a kinesin dimer with one of its heads in the ATP state attached to a tubulin dimer, see **Fig. 3(a)**. Within 50 ns of simulation, a large conformational change has occurred, see **Fig. 3(b)**. This study opens the perspective to investigate the mechanical step of kinesin at tubulin, the so-called "power stroke", in full atomic detail.

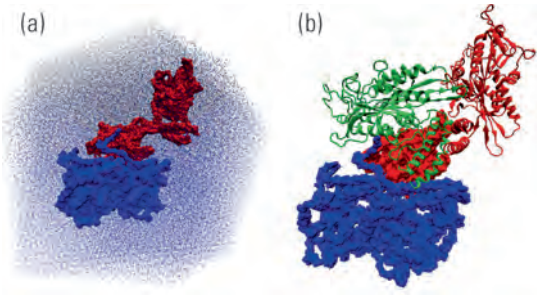

Fig. 3: Modelling the kinesin dimer at tubulin in atomic detail. (a) The system simulated includes a kinesin dimer (red surface) as well as an α-β tubulin dimer ("tubulin", blue surface). The initial configuration of the protein complex has been modelled based on an atomic model of a kinesin monomer at tubulin and a solvated kinesin dimer using rigid body motion and solvated in explicit water (blue dots). (b) Conformation of tubulin (blue) and bound kinesin head (red surface) as well as configuration of the unbound head before (red, ribbons) and after a 50 ns simulation (green).

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Protein Folding and Function

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Transition States in Protein Folding

A current focus of our research is the folding dynamics of small single-domain proteins **[1, 2, 3]**. Many of these proteins are 'two-state folders', i.e. proteins that fold rather directly from the denatured state to the native state, without populating metastable intermediate states. A central question is how to characterize the instable, partially folded conformations of two-state proteins, in particular the rate-limiting transition-state conformations between the denatured and the native state. These partially folded conformations are short-lived and cannot be observed directly in experiments.

However, experimental data from detailed mutational analyses of the folding dynamics provide indirect access to transition states. The interpretation of these data, in particular the reconstruction of transition-state conformations, requires simulation and modeling. The traditional interpretation of the mutational data aims to reconstruct the degree of structure formation of individual residues in the transition state. We have suggested a novel interpretation that aims at degrees of structure formation of cooperative substructures such as α-helices and β-hairpins, which resolves some of the inconsistencies of the traditional interpretation **[4, 5]**.

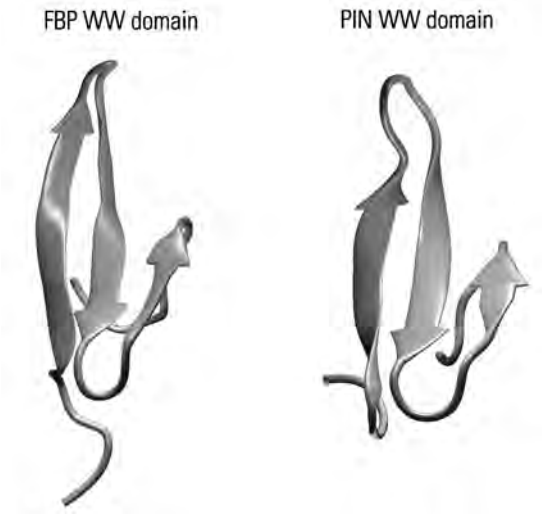

Fig. 1: The structure of WW domains consists of two β-hairpins forming a three-stranded β-sheet. The FBP and PIN WW domain shown here are two-state proteins that fold without experimentally detectable intermediate states.

The smallest β-proteins have just three β-strands. Important representatives of this class of proteins are WW domains, see **Fig. 1**, named after two conserved tryptophan residues, which are represented by the letter W in the single-letter code for amino acids. WW domains are central model systems for understanding β-sheet folding and stability. Molecular Dynamics simulations indicate that the two β-hairpins of three-stranded β-proteins are cooperative substructures.

We have analyzed the detailed mutational data for the FBP and PIN WW domains with a simple four-state model **[5]**. The central assumption of this model is that the transition state of the WW domains consists of two conformations in which either hairpin 1 or hairpin 2 are formed, see **Fig. 2**. The model has two folding routes: On one of the routes, hairpin 1 forms before hairpin 2, and on the other route, after hairpin 2. The folding rate

$$k = c\left(\mathrm{e}^{-G_1/RT} + \mathrm{e}^{-G_2/RT}\right)$$

in this model is sum of the rates for the two folding routes.

Mutations shift the free energies G_1 and G_2 of the transition-state conformations and, thus, shift the folding rate of the protein. By comparing with experimental data for the folding rates of wildtype and mutants of WW domains, we have reconstructed the transition state of these proteins. The structural information obtained from the mutational data is that the transition state ensemble of the FBP WW domain consists to roughly 3/4 of conformation 1 with hairpin 1 formed, and to 1/4 of conformation 2 with hairpin 2 formed. The transition state ensemble of the PIN WW domain consists to roughly 2/3 of conformation 1, and to 1/3 of conformation 2, according to the model.

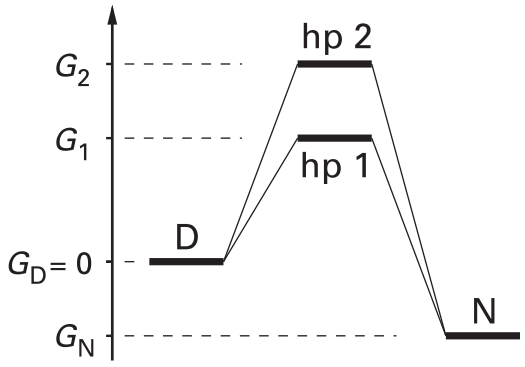

Fig. 2: Simple energy landscape of a four-state model for WW domains. The four states are the denatured state D, the native state N, and two transition-state conformations hp 1 and hp 2 in which either hairpin 1 or hairpin 2 are formed. Here, G_N is the free-energy difference between the native state N and the denatured state D with 'reference free energy' $G_D = 0$, and G_1 and G_2 are the free energy differences between the transition-state conformations and the denatured state.

Conformational Changes During Binding

The sequence of a protein determines the three-dimensional structure, in which it folds. The structure in turn enables the biological function of the protein. During their function, many proteins slightly change and adapt their three-dimensional structures. For example, the binding of a ligand molecule to a protein is often accompanied by conformational changes of the protein. A central question is whether the ligand induces the conformational change (induced-fit), or rather selects and stabilizes a complementary conformation from a pre-existing equilibrium of ground and excited states of the protein (selected-fit).

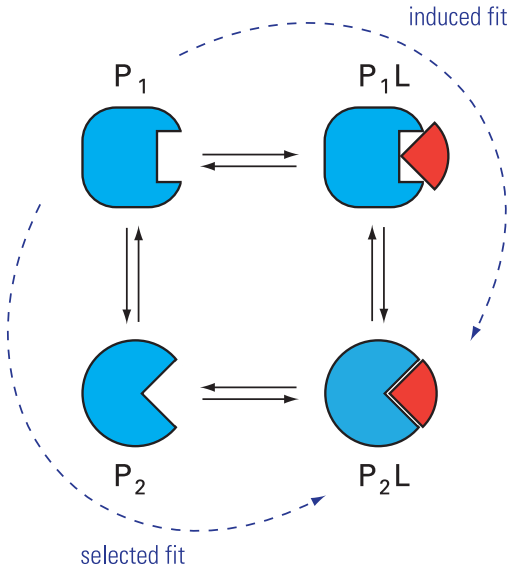

Fig. 3: Simple four-state model of protein-ligand binding. Without the ligand L, the conformation P_1 of the protein is the ground-state conformation, and P_2 is the excited-state conformation. When the ligand is bound, P_2L is the ground state, and P_1L the excited state. On the selected-fit route, the ligand binds the protein in the excited-state conformation P_2, and on the induced-fit binding route, in the ground-state conformation P_1.

We have studied the selected-fit and induced-fit binding kinetics in a four-state model of protein-ligand binding **[6]**. In this model, the protein has two dominant conformations P_1 and P_2 , see **Fig. 3**. The conformation P_1 is the ground-state conformation in the unbound state of the protein, while P_2 is the ground-state conformation in the ligand-bound state. Two routes connect the unbound ground state P_1 and the bound ground state P_2L. On the induced-fit route $P_1 \rightarrow P_1L \rightarrow P_2L$, the protein first binds the ligand in conformation P_1, which causes the transition into conformation P_2. On the selected-fit route $P_1 \rightarrow P_2 \rightarrow P_2L$, the protein binds the ligand in the higher-energy conformation P_2.

We find a characteristic difference between the selected-fit and induced-fit binding kinetics. If the conformational relaxation into the ground state is fast, the selected-fit on-rate depends on the equilibrium constant of the conformations P_1 and P_2 while the selected-fit off-rate is independent of the conformational equilibrium, see **Fig. 4**. The induced-fit on-rate, in contrast, is independent of the conformational equilibrium between P_1L and P_2L, whereas the induced-fit off-rate depends on this equilibrium. Mutations or other perturbations that shift the conformational equilibrium without affecting the shape or free energies of the binding site thus may help to identify whether a protein binds its ligand in a selected-fit or induced-fit mechanism.

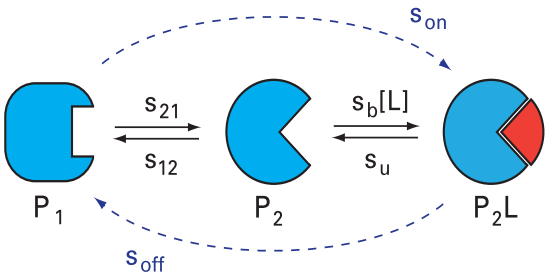

Fig. 4: Binding kinetics along the selected-fit route of the model shown in Fig. 3. Here, s_{21} and s_{12} are the rates for the conformational transitions in the unbound state, s_b is the binding rate of conformation P_2 per mole ligand, and s_u the unbinding rate. Since P_1 is the ground state and P_2 the excited state, the equilibrium constant $K_U = s_{21}/s_{12}$ for the conformational transitions in the unbound state is much smaller than 1. If the conformational transition rate s_{12} into the ground state is much larger than the binding and unbinding rates $s_b[L]$ and s_u, the on-rate along the selected-fit route is approximately $s_{on} \approx K_u\, s_b$, and the off-rate is $s_{off} \approx s_u$.

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Weak Polyelectrolytes in Poor Solvents

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Polyelectrolytes (PELs) are macromolecules that contain subgroups with the ability to dissociate charges in polar solvents such as water. PELs have received much attention because of their importance in materials science, soft matter research, and molecular biology. Weak polyelectrolytes such as poly(acrylic acid) dissociate only in a limited pH range. The total charge of the chain is not fixed but can be tuned by changing the pH. The number of charges $N_c = f\,N$ (where N is the number of monomers and f is the degree of ionization) as well as their positions along the polymer are fluctuating quantities. Therefore, weak PELs are also called annealed PELs. The imposed quantity is the chemical potential μ of charges. At high dilution, it equals the solution pH up to a trivial constant and the self energy of the released proton, $\mu = \pm \ln 10\,(\mathrm{pH}-\mathrm{pK}_0) - \lambda_B/\lambda_D$ **[1, 2]**, where pK_0 is the intrinsic dissociation constant of an isolated monomer, λ_B is the Bjerrum length that sets the strength of the Coulomb interaction, $\lambda_D = (8\pi c_s \lambda_B)^{-1/2}$ is the screening length with c_s being the salt concentration, and $\pm$ stands for bases or acids, respectively.

Many polymers are based on a hydrophobic backbone, and charged side groups often determine the solubility of PELs in water. The competition between the attractive monomer-monomer interaction due to a poor solubility of the backbone and the repulsive Coulomb interaction between the polymer charges gives rise to rather complex phase behavior of PELs in poor solvents. In the case of weak or annealed PELs in a poor solvent, the extra charge degree of freedom can have a strong effect: The chains undergo a first-order phase transition between weakly charged globules and strongly charged stretched chains **[1, 3]**. Note that the solvent quality is measured by the distance from the Θ point, $\tau = 1 - T/\Theta$. For a sufficiently poor solvent, $\tau > \tau^* \sim (u^3 N)^{-1/5}$, where $u = \lambda_B/b$ is a dimensionless interaction strength with b being the monomer size, the behavior of the polymer is dominated by this transition. However, if the system is close the Θ point, the discontinuous phase transition is suppressed and intermediate structures such as pearl necklaces can be stable **[4, 5]**.

Although the fundamental behavior of annealed PELs is determined by solvent quality and solution pH, we have demonstrated by means of computer simulations that some fine tuning of dissociation and structure can be enforced by changing the screening length **[6]**. **Fig. 1** shows the size of the polyelectrolyte in the rather-poor-solvent regime, $\tau > \tau^*$, as a function of screening length λ_D. Simulation data are taken at the maximum charge chemical potential μ at which the polyelectrolyte exhibits the transition to an almost uncharged globule. To illustrate the different configurations typical simulation snapshots are added. Hence, for constant solvent quality, interaction strength and solution pH, there is an alternative route to switch the configuration of annealed PELs by changing the ion strength of the solution. In other words, the solution pH at which an annealed PEL undergoes the discontinuous conformational transition can be adjusted by changing the concentration of salt.

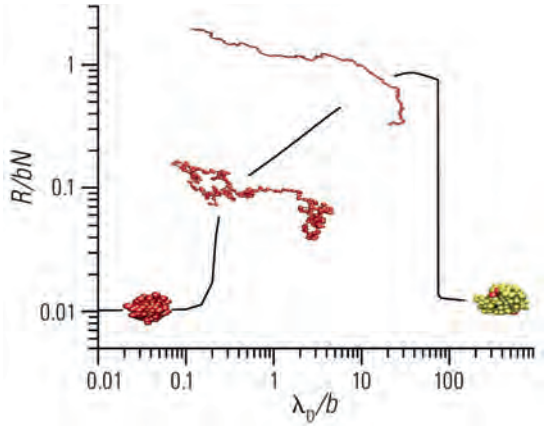

Fig.1: Rather-poor-solvent regime: Mean-square end-to-end-distance R versus screening length λ_D together with typical simulation snapshots. Charged monomers are colored red and uncharged monomers are colored yellow.

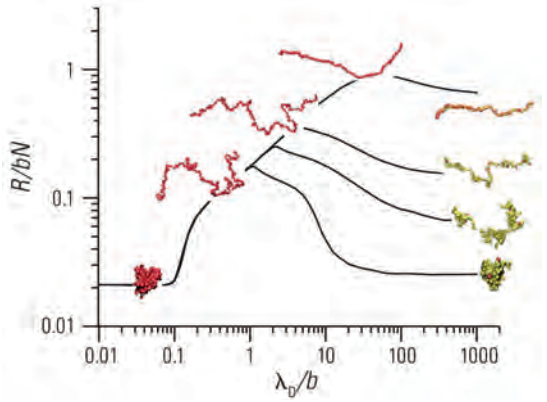

Fig. 2 Close-to-Θ-point regime: Mean-square end-to-end-distance R versus screening length λ_D at growing pH (curves from bottom to top) together with typical simulation snapshots (coloring as in Fig. 1).

In the scaling region $0.3 < \lambda_D/b < 10$, a detailed analysis shows that the polyelectrolyte behaves as a (semi-) flexible chain with persistence length $l_e \sim b(\lambda_D/b)^2$. Using the model of a flexible chain built by cylindrical monomers of length $l_e << Nb$ and diameter λ_D we find good agreement with previous theoretical predictions **[6]**. For larger screening lengths, because of the competition between growing stiffening on large length scales due to the polyelectrolyte effect on the one hand, and increasing wiggling on short length scales due to the reduced dissociation on the other hand, the end-to-end distance R exhibits an unusual non-monotonic behavior with growing λ_D.

In **Fig. 2**, we plot the same quantity as in Fig. 1, but here in the close-to-Θ-point regime, $\tau < \tau^*$. The striking difference is the absence of discrete transitions. Depending on the solution pH, continuous crossover behavior between various conformations is observed. Weakly charged pearl necklace structures first described by Dobrynin, Rubinstein and Obukhov (DRO) **[7]** appear at only low pH if the low ionization regime is reached. The population of different pearl necklace configurations can be tuned by changing λ_D see **Fig. 3**. Surprisingly pearl necklaces exist in a second region at very strong screening, but distinguished by complete ionization. In that regime, the total electrostatic interaction within a pearl is not reduced because of partial charging but due to strong screening. Obviously this mechanism is not included in the DRO theory.

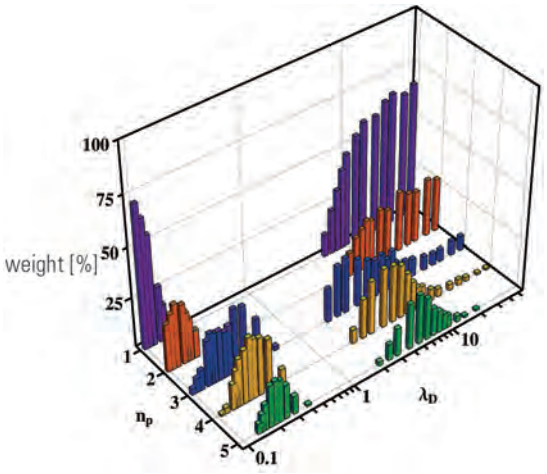

Fig. 3: Pearl necklace population at varying screening length λ_D, where n_p is the number of pearls.

By performing extensive grand canonical Monte Carlo simulations of annealed PELs in poor solvents, we have shown that variable screening can be used to establish a fine tuning of the structure of weak PELs. In **Fig. 4**, the results are combined in schematic phase diagrams in both the rather-poor-solvent regime and the close-to-Θ-point regime. In particular in the latter regime, we find a complex phase behavior of both highly and weakly charged structures.

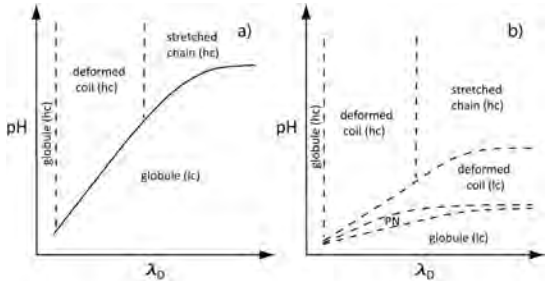

Fig. 4: Schematic phase diagram of weak PELs in poor solvent in a) the rather-poor-solvent regime and b) the close-to-Θ-point regime. The solid line in case a) indicates a first-order phase transition between high-charge states (hc) and low-charge state (lc). In case b), the hc-lc transition is a continuous one. Continuous transitions are represented by dashed lines. Note that hc globules occurring at strong screening can split into pearl necklaces (see Fig. 3) that are, however, quite different from usual DRO pearl necklaces denoted by PN.

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Motor Cycles and Operation Modes of Kinesin

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Kinesin is a motor protein that moves directly along rigid cytoskeletal filaments (microtubules) to transport intracellular cargo. The energy for this transport is supplied by the hydrolysis of adenosine-triphosphate (ATP) to adenosine-diphosphate (ADP) and an inorganic phosphate group (P). For small load forces, each individual motor step of kinesin is coupled to the hydrolysis of exactly one ATP molecule and displaces the center of mass by 8 nm towards the microtubule plus-end. The different chemical reactions and conformational transformations of a motor molecule constitute its specific chemomechanical network. The cycles of this network govern the dynamics of the molecular motor.

Catalytic Action and Processive Walk

Kinesin consists of two identical amino acid chains dimerized in a coiled coil. One end of the protein dimer binds to cargo particles, while at the other end, each of the two chains forms a globular head-domain, which is able to bind to microtubules. The motor heads do not only mediate the binding of kinesin to the microtubule track, but also contain a catalytic site for ATP hydrolysis, see **Fig. 1**.

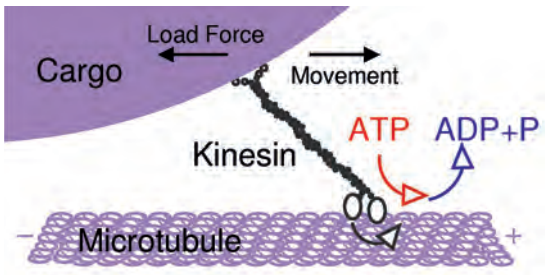

Fig. 1: The kinesin motor actively transports intracellular cargo towards the plus-end of microtubules. The motor stepping against a load force is driven by the hydrolysis of ATP to ADP and P.

The energy μ_T gained from binding an ATP molecule is partly released as $\mu_D+\mu_P$ by the unbinding of the hydrolysis products (ADP+P). The difference $\Delta\mu=\mu_T-(\mu_D+\mu_P)$ defines the chemical energy supply that can be used to perform mechanical work $W=L\,F$ via a translation of the motor by a step length L against a load force F, see **Fig. 2**.

Conservation of energy leads to the released heat $Q=\Delta\mu-W$. We have established the thermodynamics for the cycles of chemomechanical networks for molecular motors, **[1, 2]**. As a result, we obtained balance conditions for directed cycles that serve as constraints and ensure thermodynamic consistency. The obtained relations quantitatively connect thermodynamic control parameters of the motor environment with variables of the motor kinetics.

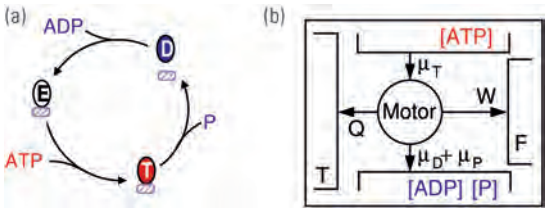

Fig. 2: (a) ATP hydrolysis cycle for an individual kinesin motor head. Each motor head may be occupied by ATP (T) or ADP (D), or be empty (E). In contrast to the E and T heads, the D heads are only weakly bound to the microtubule. (b) Energy flux diagram for a molecular motor, which is coupled to particle reservoirs with densities [ATP], [ADP], and [P], to an external load F and to a heat bath of temperature T.

Enzymatic Network Representations

The conformational state space for the dimeric kinesin molecule includes nine states as shown in **Fig. 3 (a)**. These states are connected by two types of transitions. Chemical transitions correspond to ligand binding or release events, as introduced in **Fig. 2 (a)**. Mechanical transitions correspond to the movement of the trailing motor head to the leading position, which translates the whole motor molecule by a step length L. In a systematic analysis we showed **[3, 4]**, that the main motor properties as observed in single molecule experiments by several groups as well as biochemical experiments concerning the processive walk of kinesin are described by a relatively simple model that is based on a seven state sub-network. This part of the general nine state network is composed of the three fundamental directed cycles $F1^+=|12561>$, $F2^+=|12571>$, and $B^+=|45234>$. As one can see from **Fig. 3 (b)**, the seven state network contains two additional cycles apart from the fundamental forward and backward stepping cycles, $F1^+$, $F2^+$, and B^+, namely $D1^+=|1234561>$ and $D2^+=|1234571>$. On these latter pathways the kinesin motor consumes ATP without stepping in any direction.

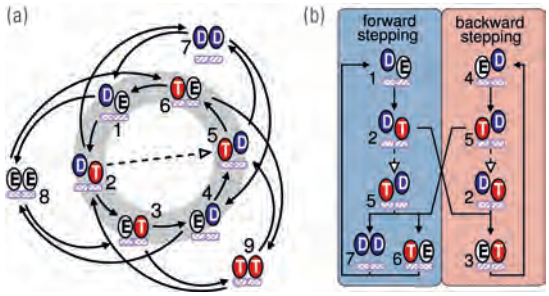

Fig. 3: (a) Network representation of the dimeric kinesin motor. While solid lines represent chemical transitions (with arrows indicating the ATP hydrolysis direction), the dashed line represents a mechanical transition (where a forward step corresponds to traveling of the weakly bound trailing head to the leading position). (b) The relevant seven state sub-network for the processive walk of kinesin.

Motor Velocity and ATP Hydrolysis Rate

The dynamics of the motor molecule is determined by excess fluxes $\Delta J(C^+)$ for each directed cycle C^+ of its chemomechanical network. In the seven state network, the motor velocity is given by $v=L(\Delta J(F1^+)+\Delta J(F2^+)-\Delta J(B^+))$, whereas the ATP hydrolysis rate is obtained from $h=\Delta J(F1^+)+\Delta J(F2^+)+\Delta J(B^+)+2(\Delta J(D1^+)+\Delta J(D2^+))$. The dicycle excess fluxes are functions of the rates that characterize each transition of the motor network. Because the transition rates by themselves depend on the three concentrations [ATP], [ADP], and [P] as well as on the load force F, the excess fluxes and consequently the motor velocity and the ATP hydrolysis rate become functions of these four thermodynamic control parameters. For fixed product concentrations [ADP] and [P], the motor velocity and hydrolysis rate can be expressed as functions of the load force and the chemical potential difference $\Delta\mu=\ln(K^{eq}[ATP]/([ADP][P]))$, where K^{eq} is the equilibrium constant for ATP hydrolysis, see **Fig. 4**. While the zeros of the motor velocity $v(F_s, \Delta\mu)=0$, for a given chemomechanical potential difference $\Delta\mu$, define the stall force F_s, the zeros of the ATP hydrolysis rate $h(F, \Delta\mu_b)=0$, for a given load force F, define the balancing chemical potential difference $\Delta\mu_b$.

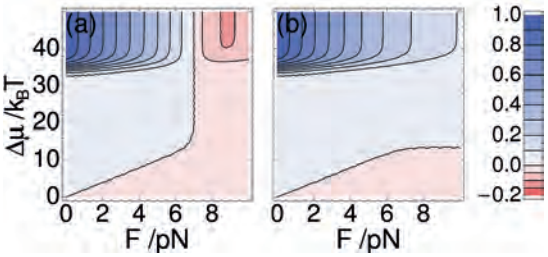

Fig. 4: (a) Motor velocity v and (b) ATP hydrolysis rate h as functions of load force F and chemical potential difference $\Delta\mu$ for fixed product concentrations [ADP]=[P]=0.5μM. Shown are the relative values with respect to $v(F=0, \Delta\mu\to\infty)$ and $h(F=0, \Delta\mu\to\infty)$.

Operation Mode Diagram for Kinesin

In **[5]** we derived explicit results for the stall force $F_s(\Delta\mu)$ and the balancing potential $\Delta\mu_b(F)$. It turned out that the dependence of the latter two quantities on the hydrolysis product concentrations [ADP] and [P] is rather weak for the relevant scales. While the stall force separates forward and backward stepping modes, the balancing potential separates ATP hydrolyzing and ATP synthesizing modes of the motor. In this way the (F, $\Delta\mu$) plane is divided up into four operation mode regions, see **Fig. 5**.

The operation mode diagram displayed in **Fig. 5** predicts for example, that the stall force F_s increases linearly with the chemical potential difference for $\Delta\mu<\Delta\mu_b(F\to\infty)=14\,k_BT$, but remains constant for larger $\Delta\mu$. Moreover, ATP synthesis against a positive chemical potential difference $\Delta\mu$ by pulling the kinesin motor into the backward direction can only be induced in the small $\Delta\mu$ regime. Thus, the operation mode diagram of the seven state network for kinesin provides explicit predictions that can be tested by future experimental studies.

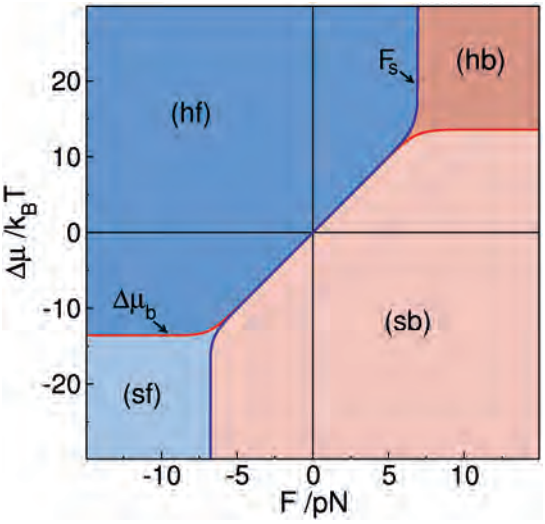

Fig. 5: Operation modes of the kinesin motor in the (F, $\Delta\mu$)-plane. The stall force F_s (blue line) separates forward and backward stepping modes. The balancing potential $\Delta\mu_b$ (red line) on the other hand, separates ATP hydrolyzing and synthesizing modes.

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Cooperative Transport by Molecular Motors

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The complex internal structure of cells depends to a large extent on the targeted transport of vesicles, organelles and other types of cargo. This traffic is powered by molecular motor proteins that can be thought of as cellular 'nano-trucks' and transport cargo along cytoskeletal filaments, the cellular 'roads'. These filaments possess an intrinsic direction: they have a 'plus' and a 'minus' end. Some motors such as kinesin-1 walk to the plus end, while others such as cytoplasmic dynein walk to the minus end. Unlike trucks, however, the molecular motors constantly undergo thermal collisions with water molecules and therefore fall off their track after a certain distance. This run length is typically of the order of 1 µm.

Motors Team up to Pull a Cargo

In the cell, molecular motors work in teams, i.e. a single cargo is usually transported by more than one motor. For example, a cargo may be transported by several kinesin motors as depicted in **Fig. 1(a)**. Because of thermal collisions with water molecules, the motors unbind from and rebind to the filament in a stochastic manner. This means that the number of motors pulling the cargo fluctuates in time. We have studied the transport of a cargo pulled by several motors both theoretically and experimentally **[1, 2]**. In a biomimetic in vitro experiment, we monitored beads pulled by several kinesins. The number of kinesins on the beads was changed in a controlled manner by incubating the beads in solutions with varying kinesin concentration c, which is directly proportional to the average number of kinesin on the bead.

The main effect of a larger number of motors is an increase in the run length of the cargo, see **Fig. 1(b)-(h)**. The intuitive reason for this increase is that, when one motor unbinds from the track, the other bound motors still provide a connection between the cargo and the filament, and give the unbound motor a chance to rebind to this filament. We have successfully fitted our experimental results with our theoretical model, see the lines in **Fig. 1(b)-(h)**. This allowed us to determine the maximal number of motors pulling the beads to vary between two and seven motors for the concentrations shown in **Fig. 1**.

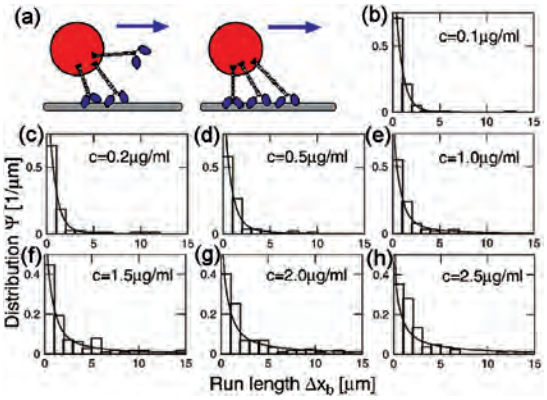

Fig. 1: Cargo transport by several kinesin motors. (a) A (red) cargo is pulled by three (blue) kinesins which unbind from and bind to the filament in a stochastic manner. (b)-(h) Experimental run length distributions (histograms) and theoretical fits (lines) for varying kinesin concentrations c. The probability of higher run lengths increases with concentration c.

Motors Play Tug-of-War

In the cell, many cargoes travel back and forth along cytoskeletal filaments, changing direction every few seconds. Since one type of motor can walk only into one direction, two types of motors must be present on such bidirectional cargoes. Indeed, cellular cargoes are often transported by several plus-end moving kinesins and several minus-end moving dyneins. This leads to the problem of coordinating motors that walk into opposite directions, see **Fig. 2(a)**. Naively, one would expect that the motors should block each other, leading to almost no cargo motion as depicted in **Fig. 2(d)**. However, cellular cargoes are observed to move rapidly back and forth as shown in **Fig. 2(e)**. This transport pattern implies that during plus motion, only plus motors are active **(Fig. 2(b))** and during minus motion, only minus motors are active **(Fig. 2(c))**. How is this cooperation accomplished?

In order to explain the observed bi-directional transport, several groups have postulated a coordination machinery that organizes the motors into states (b) and (c) and prevents state (a) in **Fig. 2**. However, we have recently developed a model which can explain the experimental observations without such an extra machinery **[3, 4]**. In our model, the motors manage to organize themselves by playing tug-of-war: The plus motors pull on the minus motors and vice versa. This force leads to an increased tendency of the motors to drop off the filament.

If, for example, more plus than minus motors are bound to the filament, the force on each minus motor is higher than the force on each plus motor. This higher force increases the probability for a minus motor to unbind from the filament. As soon as one minus motor has unbound, the remaining bound minus motors have to sustain the plus motor's force alone. This increases the unbinding probability of the minus motors even further and leads to a cascade of minus motor unbinding events until no minus motor is left – the cargo ends up in a state with only plus motors bound, as shown in **Fig. 2(b)**, and quickly moves into the plus direction. This plus motion persists until the stochastic unbinding and binding events of the motors lead to a cargo state for which more minus than plus motors are bound to the filament. Then an unbinding cascade of the plus motors leads to a state with only minus motors bound, see **Fig. 2(c)** and therefore to fast minus motion. In total, the cargo stochastically switches between fast plus and minus motion, see **Fig. 2(e)**. Our tug-of-war model can thus explain the experimentally observed bi-directional motion without postulating an unknown coordination machinery.

We have compared the results of our model to experiments on the transport of lipid droplets in fly embryos performed by Steven Gross and co-workers from the University of California in Irvine, USA. Our model was able to explain their experimental observations quantitatively.

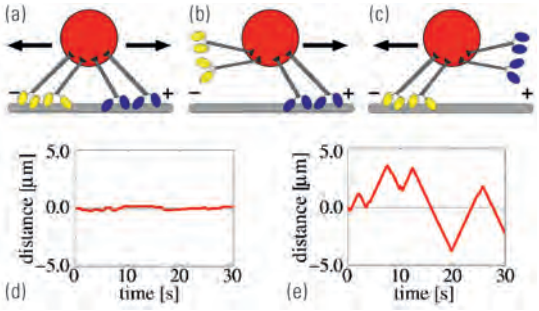

Fig. 2: Tug-of-war of molecular motors. (a)-(c) A (red) cargo particle is transported by two (blue) kinesins moving to the plus end (right) and two (yellow) dyneins moving to the minus end (left). In (a), the opposing motors block each other, so that the cargo has essentially zero velocity, as shown by the trajectory in (d). In (b) and (c), by contrast, only one type of motors is bound and can move the cargo quickly to the plus or minus end, respectively. A cargo alternating between states (b) and (c) moves quickly back and forth as shown in (e).

Motor Traffic with Internal States

If many molecular motors walk along the same filament, the traffic may become congested. We have studied this situation theoretically, taking into account that stepping of a molecular motor is a complex process which consists of a series of transitions between different motor states **[5]**. We have considered the simplest case of two internal states.

We have found that even for only two internal states, some properties of the motor traffic exhibit a strong and surprising dependence on the detailed kinetics of the step. For example, the effective unbinding rate of the motors may both increase and decrease with increasing motor density, see **Fig. 3(a)**. Likewise, the run length either exhibits a strong decrease or almost no dependence on the motor density, see **Fig. 3(b)**. These results may help to clarify controversial experimental results on motor unbinding rates and run lengths for high motor densities.

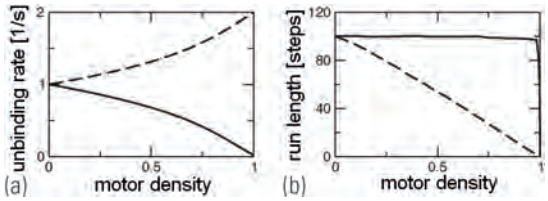

Fig. 3: Molecular motor traffic with internal states: (a) Unbinding rate and (b) run length as a function of motor density, which can vary between 0 and 1. Depending on the details of the stepping kinetics, the motors may exhibit increasing unbinding and decreasing run length (dotted lines), or decreasing unbinding and largely constant run lengths (solid lines).

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Morphologies of Vesicles Loaded with Aqueous Polymer Solution

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When a water drop is placed on a surface, it can attain the shape of a spherical cap, or it can flatten and spread. The interaction between the surface and the drop can be characterized by the contact angle. Zero or nonzero contact angle correspond to complete or partial wetting, respectively. Varying parameters such as temperature or liquid composition, one can cause the system to undergo a transition from complete to partial wetting. Examples for such transitions are not abundant. Some have been found for fluid-fluid interfaces in binary mixtures and for liquids at solid substrates. Liquid droplets at chemically patterned or topographically structured surfaces can also undergo morphological wetting transition, which reflects the freedom of the contact angles at pinned contact lines.

Recently, we discovered a complete to partial wetting transition occurring for an aqueous solution enclosed within a freely suspended lipid vesicle **[1]**. Here the substrate is a lipid membrane, permeable to water and with the thickness of a few nanometers.

Lipid vesicles have long been recognized as models for the cell membrane and have been widely used to study the properties of lipid membranes **[2]**. Recently, it has been found that giant unilamellar vesicles loaded with aqueous solutions of water-soluble polymers may exhibit several spatial compartments formed by phase separation within the vesicle interior. Thus, these artificial cell-like systems are a biomimetic setup for studying molecular crowding, fractionation and protein sorting in cells.

To study wetting transitions in vesicles, we encapsulated a homogeneous aqueous solution composed of poly(ethylene glycol) (PEG) and dextran in giant vesicles made of dioleoylphosphatidylcholine (96 mol %), and G_{M1} ganglioside (4 mol %). In order to obtain vesicles containing two phases, the vesicles were deflated osmotically by adding a hypertonic solution to the external medium in a stepwise manner.

Partial-to-Complete Wetting Transition

The polymer solution loaded in the vesicles is in the one-phase state at room temperature **(Fig. 1A)**. As the osmolarity of the external medium is increased, water is forced out of the vesicle in order to balance the resulting osmotic pressure. As a result, the polymer concentration inside the vesicle is raised and phase separation occurs **(Fig. 1B)**. Since the dextran-rich phase is heavier than the PEG-rich phase, the newly formed spherical dextran-rich droplet is always located at the bottom of the vesicle **(Fig. 1C)**. As the osmolarity of the external medium is further increased, the dextran-rich phase starts to wet the membrane **(Fig. 1D)**. The contact area between the dextran-rich phase and the membrane grows with increasing osmolarity; see **Fig. 1D-F**. The morphology change of the dextran-rich droplet indicates a wetting transition from complete wetting of the PEG-rich phase or complete dewetting of the dextran-rich phase in **Fig. 1B, C** to partial wetting in **Fig. 1D-F**.

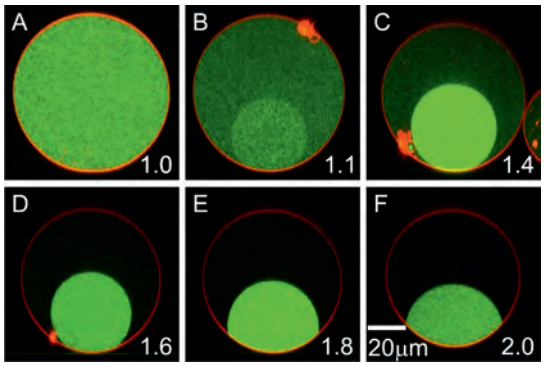

Fig.1: Confocal micrographs of a vesicle (vertical cross sections), encapsulating polymer solution with of 4.05 wt % PEG, Mw = 8 kg/mol, and 2.22 wt % dextran, Mw = 400 - 500 kg/mol. 0.52 wt % of the total dextran is labeled with fluorescein isothiocyanate (green). The membrane is labeled with 0.1 mol % dipalmytoylphosphatidylcholine-rhodamine (red). Initially, the polymer solution inside the vesicle is in the one-phase state (A). The vesicle is subjected to hypotonic solution and deflates inducing phase separation (B, C). Upon further deflation, the dextran-rich drop (green) undergoes wetting transition (D-F). The numbers on the snapshots indicate the osmolarity ratio between the external medium and the initial internal polymer solution. The system was left to equilibrate for at least 2 hours after each consecutive osmolarity change.

The overall vesicle shape seems to remain spherical during the deflation steps. The volume of the vesicle decreases with increasing osmolarity. The excess membrane area gained in this way forms a cluster of interconnected small vesicles and lipid aggregates partially visible in **Fig. 1B, C, D**.

Fitting the vesicle and the drop contours in the acquired images with spherical caps, allows us to obtain the vesicle volume under different osmolarity conditions. Because the membrane is not permeable to the polymers, the number of polymer molecules inside the vesicle is fixed and the decrease of vesicle volume is due to the loss of water. Thus, we can calculate the total polymer concentration in the vesicle at different osmolarities. In addition, the vesicle geometry allows us to measure the contact angle Θ, between the dextran-rich phase and the membrane (see inset in **Fig. 2**). The cosine of the contact angle Θ, defines the wettability via $\cos(\Theta) \equiv (\Sigma_{pm} - \Sigma_{dm}) / \Sigma_{pd}$, where Σ_{pm}, Σ_{dm} and Σ_{pd} are the interfacial tensions at the interfaces between the PEG-rich phase and the membrane (pm), the dextran-rich phase and the membrane (dm), and the PEG-rich phase and the dextran-rich phase (pd). The wettability as a function of the total polymer concentration inside the vesicle is given in **Fig. 2**. A sharp change in the contact angle is observed for polymer concentration 8.5 wt %, indicating a wetting transition.

After this transition point, the wettability of the dextran-rich phase increases with the polymer concentration as shown in **Fig. 2**.

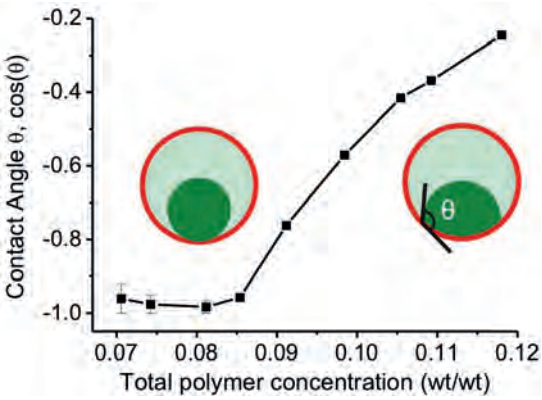

Fig. 2: The cosine of the contact angle Θ (see the right inset for definition) versus the total polymer concentration in the vesicle. The weight ratio between dextran and PEG is 0.55. The insets schematically illustrate the dewetted and wetted states.

We consider a possible mechanism involved in the observed wetting transition. When the polymer solution is close to the mixing point, the composition difference between the phases is very small, which leads to extremely low interfacial tension Σ_{pd}. When the latter is smaller than $|\Sigma_{pm}-\Sigma_{dm}|$, the membrane is fully wetted by the PEG-rich phase. Both Σ_{pd} and $|\Sigma_{pm}-\Sigma_{dm}|$ increase with increasing polymer concentration, but Σ_{pd} increases faster than $|\Sigma_{pm}-\Sigma_{dm}|$ because the compositions of both phases change, but the composition of the membrane does not. When $\Sigma_{pd}=|\Sigma_{pm}-\Sigma_{dm}|$, the wetting transition occurs, and the dextran-rich phase starts to wet the membrane. Vesicle simulations based on dissipative particle dynamics may offer a possible way to reveal the order of this wetting transition. Work in this direction is in progress.

Wetting-Induced Budding

When both phases wet the membrane, the smaller one may bud out of the vesicle body upon further deflation. **Fig. 3** shows such an example. The vesicle with two liquid phases is approximately spherical at low osmolarity ratio between the external medium and the initial internal polymer solution; see **Fig. 3B**. When the vesicle is further dehydrated, the dextran-rich phase starts to form a bud away from the PEG-rich phase; see **Fig. 3C**. The excess area arising from dehydration is utilized by the vesicle to undergo morphological changes. In this way, the area of the liquid two-phase interface is decreased significantly. As the osmolarity of the medium is increased further, the dextran-rich phase may form a complete bud leading to a dumbbell-like vesicle where the area of the two-phase interface is almost zero.

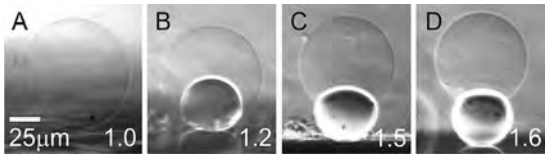

Fig. 3: Side-view phase contrast images of a vesicle sitting on a glass substrate. After phase separation (A, B), further deflation causes the dextran-rich phase to bud out (C, D). The dense part at the lower part of the vesicle is the dextran-rich phase. The light part is the PEG-rich phase. Note that the dextran was not fluorescently labeled in this vesicle as in Fig. 1. The numbers on the snapshots indicate the osmolarity ratio between the external medium and the initial internal polymer solution. The system was left to equilibrate for at least 2 hours after each consecutive osmolarity change.

The presence of the interfacial tension Σ_{pd} causes a pulling force on the membrane towards the vesicle interior. When Σ_{pd} is small, the membrane tension can easily balance this pulling in the normal direction. The excess area arising from dehydration can be stored in the form of lipid aggregates or tethers **[3, 4]**, and the vesicle can remain spherical. As Σ_{pd} increases and the vesicle deflates further (creating more excess area), the membrane tension can no longer sustain the spherical vesicle shape. Because the membrane is very flexible it bends along the interface of the liquid phases and budding of the dextran-rich phase occurs as the vesicle is further deflated. The budding event significantly reduces the interfacial energy by decreasing the contact area between the liquid phases.

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Morphological Transitions of Vesicles in AC Electric Fields

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Electromagnetic fields are widely generated by power transmission lines, home appliances and electronics for telecommunication. Thus, our bodies are always exposed to them. This raises the question: "How do biological cells react to electromagnetic fields?" Giant vesicles provide an excellent model system for the cell because their typical size (~10 µm) is of the same linear order and their fundamental structure presents a closed compartment encapsulated by a lipid bilayer membrane. The cell-size dimensions of giant vesicles allow us to observe them directly by optical microscopy. Furthermore, it is possible to systematically change the salinities of the internal and external solutions of the vesicles. Studies of giant vesicles exposed to alternating (AC) electric fields are a good start to clarify the interactions between biological cells and electromagnetic fields from the viewpoint of physics and chemistry **[1]**.

In AC electric fields, spherical vesicles can assume different shapes: spheres, prolate ellipsoids, and oblate ellipsoids. Recently, we reported the morphologies of the vesicles for a wide range of field frequencies **[1, 2]**. We found that the conductivities of the solutions had an important influence on the shapes of the vesicles and mapped those on a morphological diagram as a function of the field frequency and conductivity condition. The latter was characterized by the ratio of the conductivities of the internal vs. the external solutions: $x=\lambda_{in}/\lambda_{ex}$. On the basis of the experimental findings, we have theoretically clarified the mechanisms of the four types of morphological transitions discovered in the experiments **[3-5]**.

Experimentally Determined Morphological Transitions

Giant vesicles made of the conventional egg lecithin were prepared with different conductivity of the internal and external solutions, i.e. various conductivity ratios x. The vesicles were spheres in the absence of AC fields. They were subjected to AC fields systematically varying the field frequency ω. The vesicle deformation was visualized with phase contrast microscopy.

Fig. 1 shows the obtained morphological diagram of the vesicle shapes in AC fields. The vesicles are spheres at high frequency independent of the conductivity ratio x. When x>1, the spherical vesicles are deformed into prolates with decreasing frequency. The frequency of this transition is about 1-10 MHz, see transition 1 in **Fig. 1**. The vesicles remain prolate when decreasing the frequency further for x>1. On the other hand, when x<1, the spherical vesicles at high frequency change their shapes to oblates with decreasing frequency. The characteristic frequency of this transition is about 10 MHz (transition 2). The vesicles remain oblate in the frequency range from about 10 kHz to about 10 MHz. Note that for x>1, the vesicles are prolate in the same frequency range. Thus, there is a morphological transition at $x \cong 1$ from oblate to prolate in the course of increasing x while keeping the frequency constant (transition 3). When further decreasing the frequency, the oblate vesicles for x<1 change to prolates at the transition frequency of about 1 kHz (transition 4).

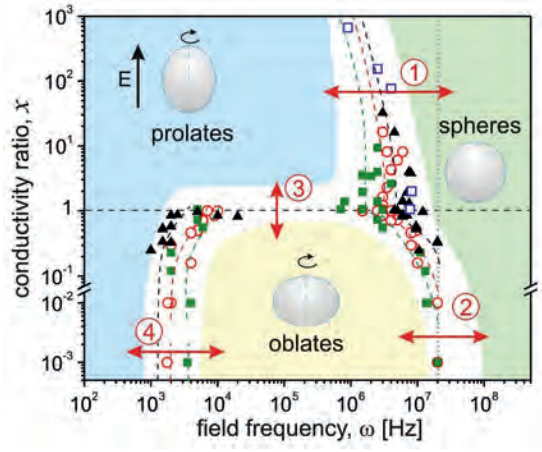

Fig. 1: Morphological diagram of giant vesicles in AC electric fields for a wide range of conductivity conditions and field frequencies. The conductivities of the internal solutions are fixed to 1.5 mS/m (filled squares), 6.5 mS/m (open circles), 13 mS/m (filled triangles), and 1000 mS/m (open squares). The broken lines are just a guide to the eye and the shaded areas indicate zones of specific morphology. The limit of the experimentally accessible frequency (2×10^7 Hz) is indicated by the dotted vertical line.

Theoretically Predicted Shape Deformations

The conductivities and the field frequency determine the conduction currents and displacement currents through the system, respectively. We have studied the mechanisms of the morphological transitions from the point of view of the current flow through the system. The developed approach extends a previous model (Winterhalter and Helfrich, J. Coll. Interf. Sci. 122, 1987) to include the effect of asymmetric conductivity conditions and the frequency dependence of the conductivity **[3-5]**. Analytical expressions of the transition frequency were derived **[4]**. The theoretically calculated morphological diagram, plotted in **Fig. 2**, agrees well with the experimental observations as shown in **Fig. 1**.

In the low frequency regime, the shapes of the vesicles are prolate independent of x. Lipid membranes are insulators, and both conduction currents and displacement currents flowing across the membranes are negligible in the low frequency regime (ω<1 kHz). As a result, the electric fields are tangential to the surface of the vesicles and do not penetrate into the vesicle interior but avoid the high impedance membrane. Maxwell stresses arise from the tangential electric fields and squeeze the vesicles at the equator: the vesicles are deformed into prolates.

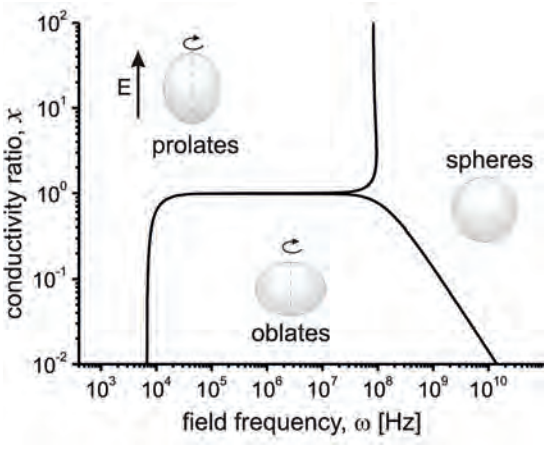

Fig. 2: The morphological diagram of vesicles in AC electric fields predicted theoretically. The calculation was carried out for vesicles with radius 20 µm. The membrane was assumed to have thickness of 4 nm and bending stiffness of 2×10^{-19} J. The conductivity of the internal solutions is 6.5 mS/m [4].

With increasing frequency, the displacement currents across the membrane grow together with the component of the electric field normal to the vesicle surface. In the intermediate frequency regime, this normal component generates shear Maxwell stresses. The latter compete with the Maxwell stresses, which deform the vesicles into prolates in the low frequency regime. The shear Maxwell stresses arising from the normal electric fields are the origin of the prolate-oblate transition 4 in **Fig. 1**.

In the intermediate frequency regime, electric charges accumulate at the interfaces of the vesicles because of the normal electric fields. The electric charge density and the corresponding net charges across the membrane depend on the conductivity condition. Within the continuum theory, these charges arise from the discontinuity of the permittivities across the interfaces and represent local accumulation of cations and anions at these interfaces. **Fig. 3** gives schematic snapshots of the electric charge distributions. They experience forces by the tangent electric fields denoted as f in **Fig. 3**. This force acts parallel to the tangent electric fields to deform the vesicles into prolates when $x>1$, and perpendicular to the tangent electric fields to deform the vesicles into oblates when $x<1$. The flip of polarity of the electric charges at $x \sim 1$ provides the mechanism of transition 3 in **Fig. 1**.

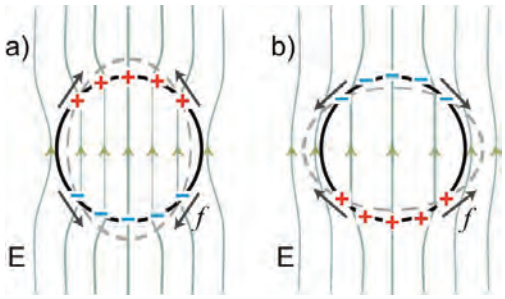

Fig. 3: At intermediate frequencies, electric charges accumulate at the vesicle interfaces. Due to the difference in the conductivity conditions, the net charges across the membrane (illustrated with pluses and minuses) differ depending on the value of x. The force applied to the charges by the tangential electric fields (f) deforms the vesicles (a) into prolates for x>1 and (b) oblates for x<1, which leads to transition 2 in Fig. 1.

In the high frequency regime, the shapes of the vesicles are spherical independent of x. The time required to charge the vesicles is characterized by the Maxwell-Wagner charging time. For higher frequency, the net electric charges across the membrane interface decay with the field frequency, and at frequencies larger than the inverse Maxwell-Wagner charging time, the electric charges cannot follow the oscillation of the electric fields. This changes the shapes of the vesicles from prolate ($x>1$) or oblate ($x<1$) to spherical, see transition 1 and 2 in **Fig. 1**.

In summary, the distributions of the electric fields by the displacement currents and the electric charges accumulated by the Maxwell-Wagner mechanisms play important roles in the morphological transitions of vesicles in AC electric fields.

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Lipid Flow Patterns in Vesicles

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When applied to colloidal systems, electric fields induce various phenomena, which have found wide application in micro- and nano-technologies in the past decade. Neutral particles (droplets, bubbles, lipid vesicles, solid beads) suspended in a medium of different polarizability acquire charge at their surfaces when exposed to electric fields. The interaction of the field with the surface charges results in a surface force that may cause particle deformation, kinetic effects, electro-osmotic fluid flows, etc.

In the case of uniform electric fields applied to lipid vesicles, the radial component of the electric surface force leads to a shape deformation at weak field strengths (see section "Morphological transitions of vesicles in AC electric fields" on page 122) or causes membrane rupture, at strong fields **[1]**. The lateral component, on the other hand, may induce fluid flows, analogous to the flows induced in liquid droplets. However, there is a fundamental difference between droplets and vesicles, which arises from the properties of the lipid bilayer. The membrane behaves as a two dimensional nearly incompressible fluid. It develops tension to keep its surface area constant.

Under homogeneous alternating (AC) fields, membrane flow in the vesicle is not expected because the lateral electric stress is counterbalanced by the resulting axially symmetric gradient in the membrane tension. In inhomogeneous fields however, this force balance is broken and a flow of lipids occurs in order to restore it. Note that in most experimental chambers and conditions used for electro-manipulation, vesicles, cells or other particles experience inhomogeneous fields, due to screening by neighbors, sedimentation, chamber geometry, or other factors.

To study the membrane dynamics in AC fields, we used giant vesicles made of lipid mixtures, which at room temperature phase separate into liquid ordered (Lo) and liquid disordered (Ld) phases. The membrane was composed of saturated and unsaturated lipids and cholesterol; for more information on the vesicle preparation see **[2]**. A tiny fraction of fluorescent dye was added, which preferentially partitions in the Ld phase. The lipid ratio was such that the Lo phase appeared as dark circular patches in the surrounding fluorescently labeled Ld phase.

The membrane flow pattern was resolved by following the motion of the Lo patches with confocal microscopy. The bottom and the top part of the vesicle were recorded as shown on the micrographs in **Fig. 1 a-c**. The inner and outer vesicle solutions were 0.1 M sucrose and glucose, respectively. This ensures an osmotic balance, i.e. constant vesicle volume, and causes the vesicles to sediment at the bottom of the chamber since sucrose solutions have higher density than glucose solutions with the same concentration. The electric field was applied between two parallel cylindrical electrodes. The proximity of the bottom glass to the vesicle leads to an asymmetric field distribution at its surface. The field strength is much higher at the lower vesicle part, facing the glass, than at the top part, see **Fig. 2**.

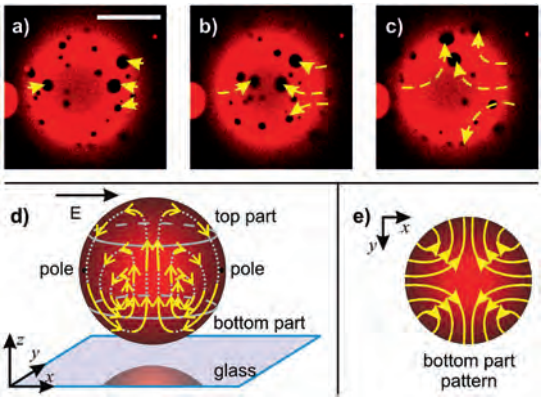

Fig. 1: Confocal micrographs illustrating the membrane flow on the bottom part (a-c) of a giant vesicle about 150 µm in diameter induced by an AC field (360 V/cm, 80 KHz), at an external conductivity of 25 mS/m. The vesicle was prepared from a mixture of 4.8 : 3.2 : 2 dioleoylphosphatidylcholine : dipalmitoylphosphatidylcholine : cholesterol. The time between the consecutive snapshots is approximately 1.3 s. The yellow dashed arrows indicate the trajectories of selected domains in the consecutive snapshots. The scale bar corresponds to 50 µm. The vesicle is located close to the bottom of the observation chamber as illustrated in (d), where the vesicle top and bottom parts, the poles and the field direction are indicated. The side and the bottom views of the flow lines are sketched in (d) and (e), respectively. The length of the arrows in (d) indicates the flow velocity.

Such asymmetric field distribution leads to a special membrane flow pattern consisting of concentric closed trajectories, organized in four symmetric quadrants, each extending from the bottom to the top of the vesicle as in **Fig. 1d, e**. The flow is fastest at the periphery of the quadrant and at the bottom of the vesicle. The top and the bottom of the vesicle are stagnation points. The velocity of the domains reaches about 30 µm/sec corresponding to laminar flows. It can be further enhanced by the field strength and the conductivity of the external solution. Interesting effects are observed when the field frequency is varied. At frequencies less than about 3 MHz, the motion in the circular trajectories is directed downwards past the poles and upwards along the equator as sketched on **Fig. 1d** but at higher frequencies it reverses its direction.

The calculation of the lateral electric stress or surface force density on the membrane suggests that the vesicle experiences larger stress in the vicinity of the solid substrate **[2]**. As a result, a non-uniform and non-symmetric membrane tension builds up. It triggers lipid flow towards the regions of highest tension, similarly to Marangoni flows in monolayers. Interestingly, the frequency at which we observe reversal of the flow direction, i.e. around 3 MHz, coincides with the Maxwell-Wagner frequency, above which the polarization of the vesicle is determined by the media permittivities. Thus, the reversal of the flow direction may arise from the difference between the permittivities of the glucose and the sucrose solutions.

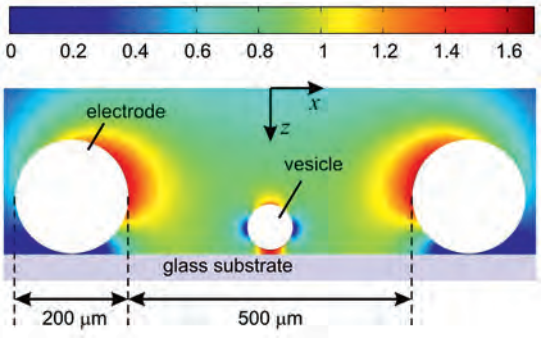

Fig. 2: Electric field distribution at 100 kHz in a cross section of the chamber consisting of two parallel cylindrical electrodes fixed to a glass substrate. The image displays a cross section passing through the centre of a vesicle located in the middle between the electrodes. The vesicle is 40 µm in radius and is located at 8 µm above the glass. The media conductivity is 0.3 mS/m. The field inside the vesicle is not shown. The data are rescaled with the strength of a field, which would be induced between two parallel planar electrodes at a distance of 500 µm.

To investigate the lipid flow driven by the electric field, we theoretically model the dielectric polarization of the vesicle by placing image electric dipoles and quadrupoles at the center of the vesicle. The calculated Maxwell stresses arising from asymmetric electric fields are found to induce flow patterns, which agree with the experimental observations **[3]**.

The flow in the membrane is coupled to fluid flows in the internal and external media. To visualize the effect of the membrane flow on the internal medium we used vesicles containing aqueous solution of the water-soluble polymers poly-(ethylene glycol) (PEG) and dextran (see section "Morphologies of Vesicles loaded with Aqueous Polymer Solutions" on page 120). At specific polymer concentration, this solution can undergo phase separation **[4]** producing droplets of dextran-rich phase, which can be visualized e.g. by fluorescently labeled dextran. The droplets tend to coarsen slowly. Before the coarsening is completed we subject such vesicles to asymmetric AC fields. As expected, the droplets start to move because of the coupling to the membrane flow. Therefore, when a cross section of the vesicle is observed with confocal microscopy as in **Fig. 3**, the droplets are observed to come into focus and to go out of focus again.

These AC field-induced flows in giant vesicles have possible applications in microfluidic technologies. Giant vesicles in inhomogeneous AC fields or in hydrodynamic flows mimicking, e.g., the situation of red blood cells in capillaries may be used as nano-reactors for fluid manipulation, i.e. displacing, mixing, trapping, etc. To demonstrate lipid mixing, we performed experiments where lipid vesicles composed of only one Lo and one Ld domains, are exposed to an AC field for a certain period of time. One example is shown in **Fig. 4**. The field-induced membrane flow causes domain fission leading to the appearance of a large number of smaller domains. For sufficiently strong membrane flows, the number of domains grows with the time of exposure. The growing number of domains, on the other hand, increases the probability of domain encounter and fusion. Domain fusion counterbalances the fission and therefore, the domains will reach a stationary state characterized by a certain size distribution after a certain time.

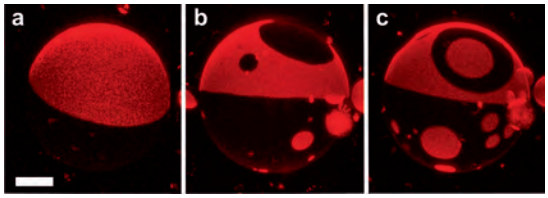

Fig. 4: 3D confocal scans of the lower vesicle hemisphere illustrating lipid mixing induced by AC field (80 kHz, 500 V/cm), at an external conductivity of 0.25 mS/m. The vesicle with a diameter about 95 µm was prepared from a mixture of 2.66 : 5.33 : 2 dioleoylphosphatidylcholine : dipalmitoylphosphatidylcholine : cholesterol. (a) Before applying the field, the vesicle has only two domains, which break apart after continuous field exposure of (b) 2 min and (c) 3 min. The scale bar corresponds to 25 µm.

We were not able to achieve similar mixing of dextran-rich and PEG-rich phases starting from a state, where the two phase are fully separated, because the pressure of the internal flow was not large enough to overcome the surface tension between the two polymer phases. However, in other systems, e.g. vesicles enclosing suspensions of micro-particles, the induced flows may be used to homogenize the internal vesicle content.

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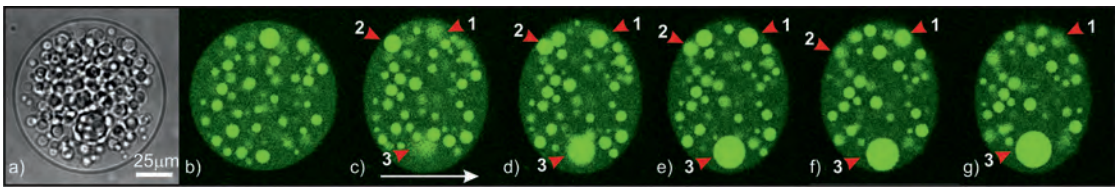

Fig. 3: (a) A phase-contrast images and (b-g) confocal cross sections of a giant lipid vesicle enclosing dextran-rich droplets (green fluorescence) in a PEG-rich phase. The cross section in (b), corresponding to the image in (a), is taken close to the equatorial plane of the vesicle and shows only the droplets in focus. Application of an inhomogeneous AC field (460 V/cm, 80 KHz) at an external conductivity of 40 mS/m leads to a vesicle shape deformation and an internal flow, in the direction perpendicular to the plane of the image in (c-d). The flow is visualized by following the motion of droplets 1, 2 and 3, which come in focus and go out of focus. The time period is 2.5 s between images c)-d) and d)-e), and 5 s between e)-f) and f)-g). The field direction is indicated by the arrow in (c).

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Membranes and Nonpolar Surfaces

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Membranes

The function of biomembranes is not restricted to surrounding a cell and its various compartments as passive separation layers. By facilitating transport of molecules from one side to the other, they play also an active role. Membranes are composed of a complex mixture of various lipids and proteins, with the lipids forming a bilayer. Our aim is to understand biomembranes in terms of the self-organization of these constituents. The information about the molecular architecture of membranes accessible experimentally is very limited. Therefore, we use molecular dynamics simulation techniques to computationally model the cooperative processes underlying the mesoscopic properties of membranes. Molecular dynamics simulations based on numerically solving Newton's equations of motion to propagate a system in time and semi-empirical force fields to describe interatomic interactions may provide highly detailed information about the molecular properties of membranes. As a first step, we model membranes as lipid bilayers, see **Figs. 1-4 [1-3]**.

Membrane fusion is a key step for important processes including viral infection and drug delivery. For the first time, we have studied the fusion of lipid vesicles in atomic detail, see **Fig. 1 [1]**. This process involves the formation of a lipidic connection between two opposed bilayers denoted as stalk, (see **Fig. 1a**) and subsequent formation (see **Fig. 1b**) and rupture (see **Fig. 1c**) of a hemifusion diaphragm. This work opens the perspective to investigate a wide range of mesoscopic biological processes at atomic resolution.

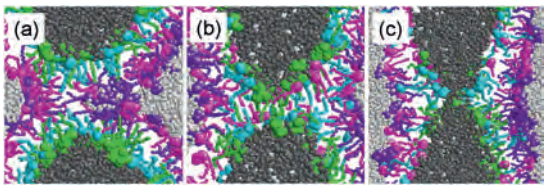

Fig. 1: Fusion of vesicles composed of dipalmitoyl-phosphateidylcholine (DPPC) and (protonated) palmitic acid (PA) in a molecular dynamics simulation in atomic detail [1]. (a) A stalk as well as a hemifusion diaphragm (b) before and (c) after rupture are depicted. Water and head group atoms are shown as spheres, tails are shown as bonds. Water is depicted in dark or light gray. Colors distinguish between DPPC (purple and green) and PA molecules and the leaflets where the molecules resided initially.

The free energy of early membrane fusion intermediates has been determined using simulations in conjunction with a coarse grained model, see **Fig. 2 [2]**. We find that the free energy of a stalk is lower than that of a pre-stalk intermediate which involves a single hydrated lipid tail. A peptide known to induce fusion in vitro does not change the free energy of stalks but does lower the free energy of the solvated tail intermediate. These results challenge assumptions of continuum models and support the idea that early fusion kinetics is determined by interbilayer flips of lipid tails.

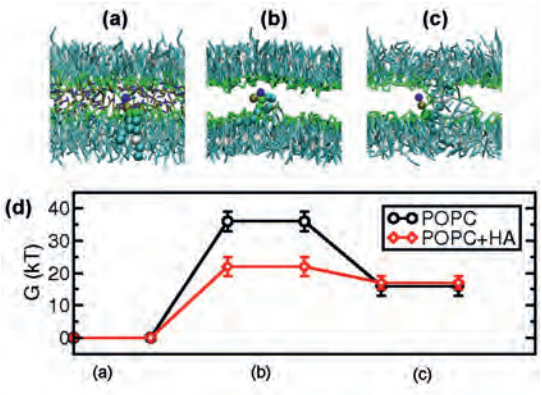

Fig. 2: Free energy of early membrane intermediates from molecular dynamics simulations in conjunction with a coarse grained model [2]. The system simulated was a palmitoyl-oleoyl-phosphateidylcholine (POPC) bilayer at low hydration fused with its periodic image (a-c). The bilayer at equilibrium (a), the transition state for interbilayer flips of a lipid tail (b), and a stalk (c) are depicted. (d) The free energies in the absence (black) and presence (red) of an influenza hemagglutinin fusion peptide are compared. In (a-c), lipids are shown as sticks and a selected lipid to which a harmonic potential was applied to induce the intermediates on the limited timescale of the simulations is highlighted. In (b,c), the choline and phosphate groups of the other lipids are omitted for clarity.

Peptides can also induce pores which is the putative mode of action of α-helical antimicrobial peptides. We are currently investigating the interaction of the antimicrobial peptide NK-2 with lipid bilayers. Membrane pores, though, can also form in the absence of peptides. In a recent study we have revealed that membrane nanopores, see **Fig. 3a**, correspond to a local free energy minimum, explaining previous data on transmembrane conductance and the metastability of nanopores observed in previous numerical studies **[3]**. In the same set of simulations, the free energy of lipid desorption, see **Fig. 3b**, has been calculated. Our results indicate that the free energies of lipid desorption from a bilayer or from a micelle differ, and that the critical micelle concentration is an inadequate reference for the energetics of lipid desorption from a bilayer unlike commonly assumed.

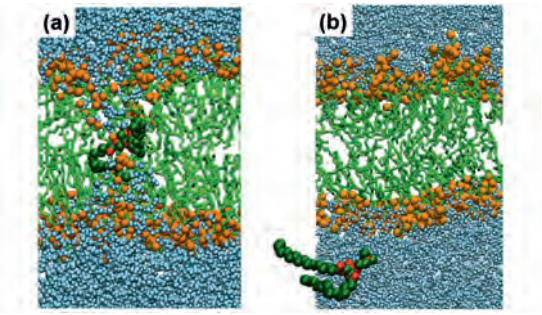

Fig. 3: The energetics of (a) nanopores and (b) lipid desorption for a DPPC bilayer were determined from atomistic simulations in which a harmonic potential was applied to a selected lipid [3]. Lipid tails are shown as green sticks and headgroups as orange spheres. The lipid subjected to the harmonic potential is highlighted. Water is shown in blue.

Understanding membranes at physiological conditions requires to investigate their interaction with ions. We are studying the interaction of potassium (K), sodium (Na), and lithium (Li) with zwitterionic phospholipid bilayers, see **Fig. 4(a,b)**. Potassium and sodium are the most abundant cations inside or outside a cell, respectively, whereas lithium intake can be curative or toxic depending on the dosage. We find that all of these cations are adsorbed at the headgroups of a zwitterionic lipid bilayer. The affinity increases in the order K<Na<Li and, thus, increases with decreasing size of the bare ion. These observations agree with results from electrophoresis experiments. In order to facilitate quantitative predictions on the affinity, an improved force field for alkali chlorides in water has been developed **[4]**. For the first time, we have used simulations to study cholesteryl hemisuccinate (CHEMS), an acidic cholesterol ester. CHEMS forms bilayers and is used as a subcomponent of liposomes for drug delivery. For CHEMS in the anionic state, the negative charge of the lipids is found to be almost fully compensated by (sodium) counterions adsorbed at the lipid headgroups, see **Fig. 4c**.

Lipid bilayers may also adsorb cationic peptides as observed for antimicrobial peptides. The antimicrobial peptide NK-2 is not only adsorbed at anionic but also at zwitterionic (phosphateidylethanolamine, PE) lipids while it does not interact with (zwitterionic) phosphateidylcholine (PC) lipids, as indicated from electrophoretic mobilities. We address the question how NK-2 distinguishes between prokaryotic and eukaryotic membranes. The hypothesis that, at physiological conditions, the underlying mechanism is not simply charge complementarity as commonly assumed but more specific molecular interactions, is currently tested.

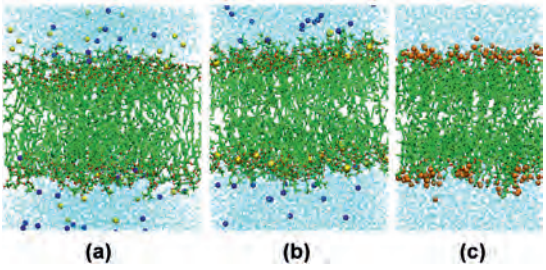

Fig. 4: Adsorption of ions to lipid bilayers. A POPC bilayer in an aqueous LiCl solution (a) before and (b) after a 100 ns simulation as well as (c) an anionic CHEMS bilayer with Na counterions after a 100 ns simulation are depicted. Lipids are shown as green sticks. Lipid oxygen atoms (red) are indicated. Ions are shown as spheres whose colors distinguish between Li (yellow), Cl (blue), and Na (orange).

Electrophoresis of Neutral Particles

Though widely used to assess the surface charge of colloidal particles, electrophoresis experiments may be misleading, as indicated by simulations in our group. For more than a century, electrophoretic mobilities of hydrophobic particles in water have been interpreted in terms of negative surface charges from the adsorption of hydroxide (OH^-). In contrast, recent spectroscopic and simulation studies have indicated significant surface affinity for hydronium (H_3O^+) but not for hydroxide. In simulations we observe that neutral wax slabs in water in the presence of an electric field but in the absence of ions migrate as though they were negatively charged, see **Fig. 5 [5]**. This work may resolve the controversy between the electrophoretic and spectroscopic studies and supports the view that neat water at hydrophobic surfaces is acidic.

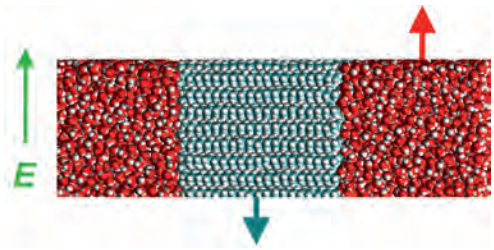

Fig. 5: Electrophoresis of neutral particles in simulations. A wax slab (hexatriacontane, C36) parallel to an external electric field in water in the absence of ions migrates as if it was negatively charged. Colors distinguish between carbons (cyan), oxygen (red), and hydrogen (white). The direction of the electric field (green) and the motion of wax (cyan) and water (red) are indicated.

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Tension Induced Membrane Fusion

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Fusion of biological membranes is an essential process in many areas of cell biology, ranging from vesicular trafficking and synaptic transmission to cell-cell fusion and viral fusion. Lipid vesicles, which are often used as simplified model systems for the rather complex biological membranes, can also be induced to fuse experimentally by a variety of methods.

Since it is currently not possible to resolve the length and time scales of membrane fusion experimentally, we use a mesoscopic simulation technique, dissipative particle dynamics (DPD), to probe the molecular details and energy barriers of the fusion process **[1-4]**. We focus on the presumably simplest way to induce fusion between a vesicle and a planar bilayer, namely via membrane tension.

The stochastic nature of the process makes it necessary to simulate a large number of fusion attempts in order to obtain reliable fusion statistics and to extract meaningful values for the fusion probability and the average fusion times.

A Molecular Picture of the Fusion Pathway

All successful fusion events follow the same pathway shown in **Fig. 1**. In this fusion pathway, configurations of individual lipids play an important role.

Upon first contact, the vesicle adheres to the planar membrane patch, forming a relatively sharp contact angle. Fusion starts with individual lipids at this 'kink' assuming a splayed tail configuration with one tail inserted in each membrane. This disturbs the local double-bilayer structure and leads to the formation of a disordered membrane domain within the contact zone where the hydrophobic regions of the two bilayers are in direct contact, and which expands following the contact line in a bean-like shape. Finally, within this disordered region, lipids reorder to form a small hemifused patch, which expands for a short time and finally ruptures at the rim to form the fusion pore.

Overall, the fusion process can be decomposed into three sub-processes. (i) Sub-process α corresponds to the first lipid tails moving into the other bilayer, (ii) sub-process β consists of the nucleation of the hemifused patch and (iii) sub-process γ corresponds to the rupture of this patch and formation of the fusion pore.

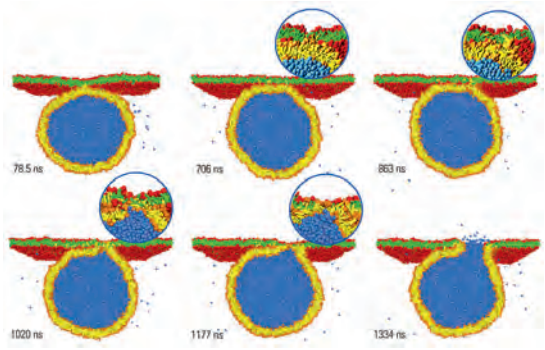

Fig. 1: Fusion of a vesicle to a planar membrane. The vesicle consists of 6869 lipids (orange heads, yellow chains), the planar membrane contains 6911 lipids (red heads, green chains). The water beads originally inside the vesicle are blue, those outside are not shown for clarity. The six snapshots illustrate the development of the fusion event from 78.5 ns after the first contact until the fusion pore opens after 1334 ns. The insets are magnifications of the lipid rearrangements at the contact line.

Fusion Probability and Alternative Pathways

When two tense membranes come into contact they may fuse. Alternatively, tense membranes may rupture or, at lower tensions, either the hemifused patch might expand without rupturing, thereby gaining membrane area and relaxing the membrane tension or the adhering state might remain stable.

Because of these other possibilities, the fusion probability depends strongly on the membrane tension as can be seen in **Fig. 2**. The probability of successful fusion is high for an optimal intermediate tension, but decreases steeply for smaller tensions as adhesion and hemifusion become more favourable. As the tension decreases, the fusion probability seems to vanish before the tensionless membrane state is attained. This would imply that the tension has to exceed a certain threshold value in order to induce fusion **[3, 4]**.

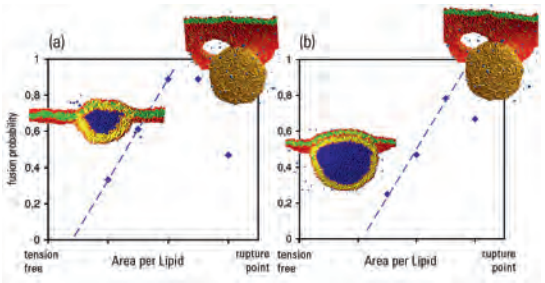

Fig. 2: Fusion probability as a function of molecular area for vesicles with a diameter of (a) 14 nm and (b) 28 nm. In both cases, the fusion probability depends strongly on the tension with a maximum at an optimal value. At higher tensions, fusion becomes less likely because of membrane rupture; at lower tensions, fusion is more and more replaced by hemifusion or adhesion.

Fusion Time Distribution and Energy Barriers

The tension determines not only the success rates, but also the time scale of fusion. At lower tensions (i) the fusion times become larger and (ii) the fusion time distributions become broader. From the statistics of the fusion time together with separate simulations in which one lipid was pulled into a splayed conformation, the energy barriers for the fusion observed in these simulations could be estimated **[2, 3]**.

Fig. 3 shows the average fusion time as a function of the molecular area. It appears to grow exponentially with decreasing tension. This exponential growth of the fusion times together with the decreasing fusion probability makes it exceedingly difficult to determine the time scale of fusion from computer simulations as the tensionless state is approached.

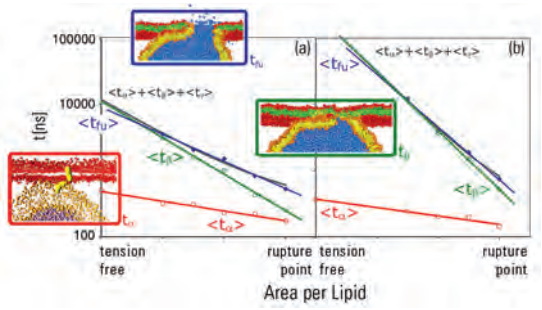

Fig. 3: The average duration of the tension dependent sub-processes α (red circles) and β (green diamonds) displayed together with the average fusion time (blue diamonds) as a function of the area per molecule for vesicles with a diameter of (a) 14 nm and (b) 28 nm. Both times depend exponentially on the area per molecule. The three insets show the final states of the sub-processes.

The average duration of the sub-processes α and β, both decrease exponentially with increasing tension, as shown in **Fig. 3**. This implies that the corresponding energy barriers should depend linearly on the membrane tension. The timescale of sub-process γ on the other hand, is found to vary between 150 ns and 300 ns, independent of both tension and vesicle size.

Since the sub-process α involves the movement of single lipids, relative to their surroundings, it is accessible to direct simulation. In two adhering membranes, a single lipid tail was pulled slowly with a harmonic potential from its original position into the other bilayer, so that the lipid assumes a splayed conformation as observed in the fusion simulations. The average work required for this process in 20 independent simulations was found to be $9 \pm 2\,k_BT$. This value constitutes an upper bound for the energy barrier and should correspond to the barrier itself for very slow pulling. Using the Jarzynski relation on this data leads to a similar barrier height of $8\,k_BT$.

The energy barrier for this process is provided by the (partially) hydrated polar head groups of the proximal monolayers. In the coarse-grained simulations it is implemented via one specific interaction parameter. Simulation enforcing a splayed lipid conformation, have shown, that the height of the barrier is primarily governed by the value of this parameter. Thus the barrier size can be tuned in such a way that it is consistent with available reference data such as the hydration energy of one hydrocarbon chain.

Using the information obtained in these simulations in the fits to the other timescales, the energy barriers corresponding to the other sub-processes for a tension free membrane can be estimated to be $10-15\,k_BT$ and $8\,k_BT$. At low tensions the total fusion time is dominated by the timescale of hemifusion. Thus the simulation statistics suggest that the main energy barrier for fusion of tensionless membranes is of the order of $10-15\,k_BT$ **[2,3]**.

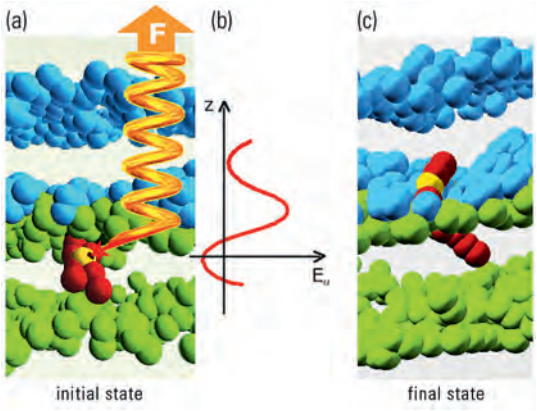

Fig. 4 Simulations of enforced lipid flips used to measure the corresponding energy barrier (a) From two adhering bilayers (head beads blue/green, tail beads omitted for clarity) a single lipid is selected (orange heads, yellow/red tails) and a force F arising from a slowly moving harmonic potential is applied to one of its tail beads (red), until the tail has flipped to the other bilayer, so that the lipid has assumed a splayed configuration with one tail inserted in each bilayer as shown in (c). (b) Energy landscape for the bead as a function of the displacement z of the yellow bead. It has a high barrier in the centre corresponding to the repulsive head groups and increases to the sides reflecting displacement of the head group into the hydrophobic region.

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Membrane Adhesion

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Biological membranes are the "skin" of cells. On the one hand, membranes separate the cell interior from the environment. On the other hand, they allow a vital exchange of matter. In addition, they are involved in central biological processes such as photosynthesis and recognition. The membranes are elastic and can attain a multitude of different shapes. The elastic properties depend on the different lipids and proteins that constitute the membranes.

Membrane Domains at Corrugated Substrates

Biological membranes contain a multitude of lipid molecules. Although the lipid molecules diffuse quickly through the fluid membranes, they are not homogeneously distributed. Instead, they tend to form domains that are either rich or poor in cholesterol. The cholesterol-rich domains are stiffer than the cholesterol-poor domains, which has direct implications on the membrane curvatures. The membrane curvatures, in turn, influence the domain formation. Curvature and domain formation thus depend on each other.

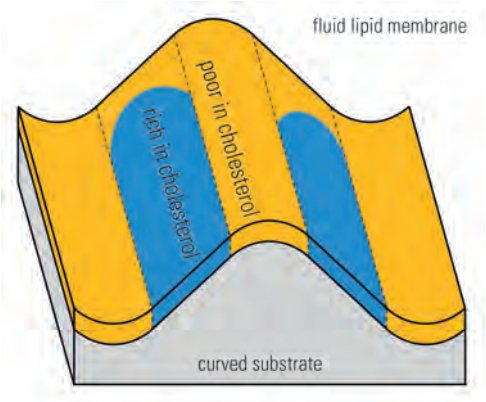

Fig. 1: Fluid lipid membrane on a corrugated, solid substrate. The membrane contains domains that are rich (blue) or poor (yellow) in cholesterol. The cholesterol-rich domains are stiffer than the cholesterol-poor domains and tend to avoid the curved parts of the membrane along the ridges and valleys of the substrate, provided the line tension between the domains does not exceed a certain threshold value.

The question now is: Can curvatures that are imposed on the membrane, e.g. by a corrugated substrate, cause stable domain patterns? In general, it is difficult to control the size of lipid domains since they readily coalesce and grow into larger and larger structures. However, if the membranes adhere to a substrate with a geometrically structured surface, the stiffer cholesterol-rich domains tend to avoid the curved parts of the membrane. The resulting domain patterns are stable as long as the curvature of the substrate surface exceeds a threshold value that depends on the line tension of the domains boundaries **[1]**. Below this threshold, a single cholesterol-rich domain forms, which covers many ridges and valleys of the substrate.

These theoretical arguments explain patterns that have already been observed in experiments. They might also help to understand why biological membranes exhibit only small domains rich in cholesterol, while in artificial, "biomimetic" membranes rather large domains are formed. In contrast to artificial membranes, biological membranes are attached to the cytoskeleton of the cell, i.e. to a network of polymers that actively curves the membranes. Besides other active cell processes, these curvatures could stabilize membrane patterns with small cholesterol-rich domains.

Interactions Mediated by Adhesive Particles

The adjustment of surface interactions is crucial for controlling the adhesiveness of biological cells and membranes. These interactions are often dominated by the composition of the membranes, but can also be affected by molecules or particles in the surrounding medium. The concentration of these particles is an additional control parameter for the membrane interactions, a parameter that is often easier to adjust than the membrane composition, and can be varied over a wider range than external parameters such as temperature.

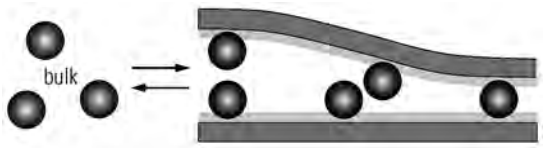

Fig. 2: Two membranes in contact with a solution of adhesive particles. A particle can bind the two membranes together if their separation is slightly larger than the particle diameter (particle on the right). At large separations, the particles can only bind to one of the membranes (particles on the left).

On the one hand, non-adhesive particles can induce attractive 'depletion' interactions between membranes or surfaces, because close contact of the surfaces reduces the excluded volume for the particles. On the other hand, adhesive particles can directly bind two membranes together if the membrane separation is equal to or slightly larger than the particle diameter, see **Fig. 2**. At larger separations, the particles can only bind to one of the membranes.

We find that the effective, particle-mediated adhesion energy of the membranes is given by

$$U_{ef} \approx \frac{k_B T}{d^2} \ln \frac{1 + q\phi e^{2U/k_B T}}{\left(1 + q\phi e^{U/k_B T}\right)^2} \qquad (1)$$

for small volume fractions Φ and large binding energies U of the adhesive particles **[2]**. Here, d is the particle diameter, T denotes the temperature, and q is a dimensionless parameter that depends on the range of the interaction between the particles and the membranes.

Interestingly, the effective adhesion energy (1) exhibits a maximum at an optimum volume fraction of the particles, see **Fig. 3**. At this volume fraction, the particle coverage of two planar parallel membranes turns out to be close to 50 % for large separations ('half coverage'), and 100 % ('full coverage') for short, binding separations. Bringing the membranes from large separations within binding separations thus does not 'require' desorption or adsorption of particles at the optimum volume fraction.

The effective adhesion energy (1) can be understood as a difference of two Langmuir adsorption free energies **[2]**. The adhesion energy can also be generalized to cases in which the adhesive particles or molecules specifically bind to receptors anchored in the membranes **[2]**. Examples are biotinylated lipids, which can be crosslinked by the protein streptavidin.

Diffusion of Receptor-Ligand Bonds

The adhesion of cells is mediated by membrane receptors that bind to complementary ligands in apposing cell membranes. It is generally assumed that the lateral diffusion of mobile receptor-ligand bonds in membrane-membrane adhesion zones is slower than the diffusion of unbound receptors and ligands. We have found that this slowing down is not only caused by the larger size of the bound receptor-ligand complexes, but also by thermal fluctuations of the membrane shape **[3]**. In our model, the fluctuations reduce the bond diffusion constant in planar membranes by a factor close to 2 in the biologically relevant regime of small bond concentrations. Active cell processes may enhance these membrane shape fluctuations **[4]**.

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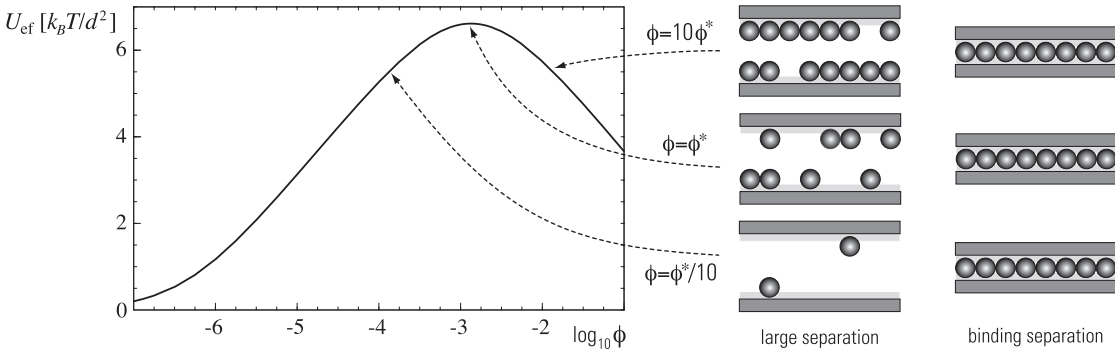

Fig. 3: Effective adhesion energy U_{ef} of the membranes, given in eq. (1), as a function of the particle volume fraction Φ for the binding energy $U = 8\,k_BT$ and $q = 0.25$. The effective adhesion energy is maximal at the optimal volume fraction $\Phi^* \approx \exp(-U/T)/q \approx 1.34\ 10^{-3}$. At the optimal volume fraction, the particle coverage of two planar parallel membranes is about 50 % for large separations, and almost 100 % for small separations at which the particles can bind to both membranes.

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Life Cycle of Chlamy Cells

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Chlamydomonas reinhardtii with the short name chlamy is a unicellular photosynthetic alga, see **Fig. 1a**, which is studied within the ongoing project GoFORSYS on systems biology. Large populations of cells are cultivated in a fermenter at the MPI of Molecular Plant Physiology, varying several environmental conditions such as light spectrum, light intensity, temperature, and nutrient concentrations. Samples of about one million cells are extracted from the fermenter to perform measurements that should shed light onto several aspects of the intracellular activity. As a result of these measurements, the metabolite concentrations are obtained as averages over a very large number of cells.

In general, the cells that contribute to these average properties differ in their age, size, and molecular composition. It is, thus, not obvious how these average quantities are related to the properties of single cells. In order to address this question, our project considers theoretical models for cell populations. As shown schematically in **Fig. 1b**, each cell undergoes a cell cycle that starts with the growth phase (G1), passes a commitment point for cell division, and then enters the other phases necessary for this division.

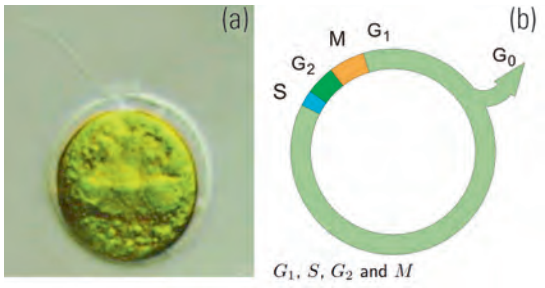

Fig. 1: (a) Image of one single cell of Chlamydomonas reinhardtii. (b) Schematic representation of the cell cycle of a single cell. The phase denoted by G1 is the growth phase; the other three phases prepare the cell for division. The phase G0 is a dormant or rest phase.

It turns out, that chlamy cells remain in the growth phase for a random amount of time and thus attain a relatively broad distribution of cell sizes. This implies that each mother cell can produce a number of daughter cells roughly proportional to its size and, thus, can undergo multiple divisions.

One global property of each cell is its volume which should determine the overall rate of energy consumption. Our first objective was therefore to develop a model for the cell size distribution under time-independent conditions that may be implemented in the fermenter. The model can be used to calculate stationary distributions, two examples are shown in **Fig. 2** corresponding to binary and multiple divisions.

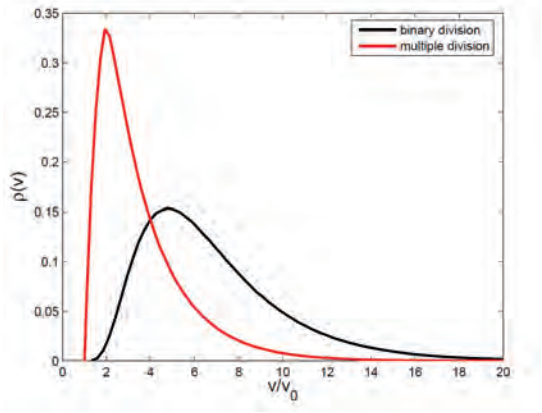

Fig. 2: Probability density for the cell volume under constant light conditions in units of the minimum volume v_0 of a viable cell. The two plots, computed with our model, compare two possible distributions assuming either binary divisions with two daughter cells or multiple divisions with more than two daughter cells as observed for chlamy cells.

Another set of experiments is performed by Martin Steup at the University of Potsdam, in which cells are synchronized by fixed periods of light and darkness. The cells are grown in a special medium that does not allow cell growth in the darkness. Synchronisation relies on the fact that, under certain general conditions, all cells would divide after the start of the dark period and the daughter cells would start to grow only when light is turned on again. By diluting the cells to a fixed density at every start of the light period and by renewing the cultivation medium, it is possible to observe the population over a long period of time under the same set of conditions.

This set-up has the advantage that both the average growth rate of the cells during the light period, the number of cells in the cultivation and, to a certain extent, the number of cell divisions can all be observed simultaneously. Moreover, during these synchronisation experiments, in which both the light and the dark periods typically last twelve hours, one can easily measure the cell size distribution of the cells. Our current aim is to adapt our model to predict the cell size distribution at the beginning of the light period.

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Activity Patterns on Networks

The biosphere contains many networks built up from rather different elements such as molecules, cells, or organisms. In spite of their diversity, these networks exhibit universal 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.

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. Many biological networks are found to be scale-free in the sense that their degree distribution behaves as

$$P(k) \sim 1/k^{\gamma} \text{ for } k > k_0$$

which defines the scaling exponent γ. Another structural property of networks is their assortativity and dissortativity. Networks are assortative or dissortative if vertices with large degree are primarily connected to other vertices with large or small degree, respectively. Biological networks tend to be dissortative.

Fig. 3: Graphical representation of the neural network of C. Elegans. The vertices correspond to sensor (S), Inter (I), and motor (M) neurons; the edges represent chemical links via synapses and electrical connections via gap junctions. The input signal is received by the S neurons, processed by the I neurons, and eventually transmitted to the M neurons.

In general, the elementary units or vertices of biological networks are dynamic and exhibit various properties or internal degrees of freedom that evolve with time. A more detailed description of the network is then obtained in terms of dynamical variables that are defined for each vertex of the network. Two examples for such dynamical processes are provided by genetic networks that exhibit a changing pattern of active and inactive genes as well as by neural networks that can be characterized by firing and nonfiring neurons. A relatively simple example for a neural network is shown in **Fig. 3** corresponding to the 302 neurons of the worm C. Elegans.

In general, the dynamics of each vertex is determined by the local interactions of this vertex with its neighbours. One instructive example is provided by local majority rule dynamics which is defined as follows: 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.

If one starts with a certain pattern of active and inactive vertices, the synchronous update of all vertices according to their local rules determines the time evolution of the activity pattern on the whole network, see **Fig. 4**. For long times, all activity patterns evolve towards one of the attractors (fixed points, limit cycles, etc) of the global dynamics.

Local majority rule dynamics has always two fixed points corresponding to two completely ordered patterns, the all-active pattern and the all-inactive one. In fact, for random scale-free networks without degree-degree correlations, these two fixed points are the only attractors of the dynamics as has been shown in previous studies. **[1]**

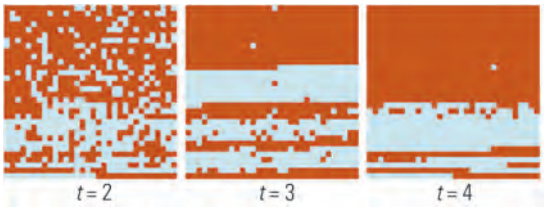

Fig. 4: Time evolution of activity pattern towards an attractor that switches back and forth between the two patterns for t = 3 and t = 4. In each panel, the vertices are arranged according to their degree starting with the smallest degree in the upper left corner and ending with the largest degree in the lower right corner.

This situation changes drastically for majority rule dynamics on scale-free networks with degree correlations. In the latter case, the activity patterns are governed by a large number of attractors. One example corresponding to a limit cycle of period two is displayed in **Fig. 4**. In fact, dissortative scale-free networks have the interesting property that the number of attractors exhibits a maximum as a function of network size. **[2]**

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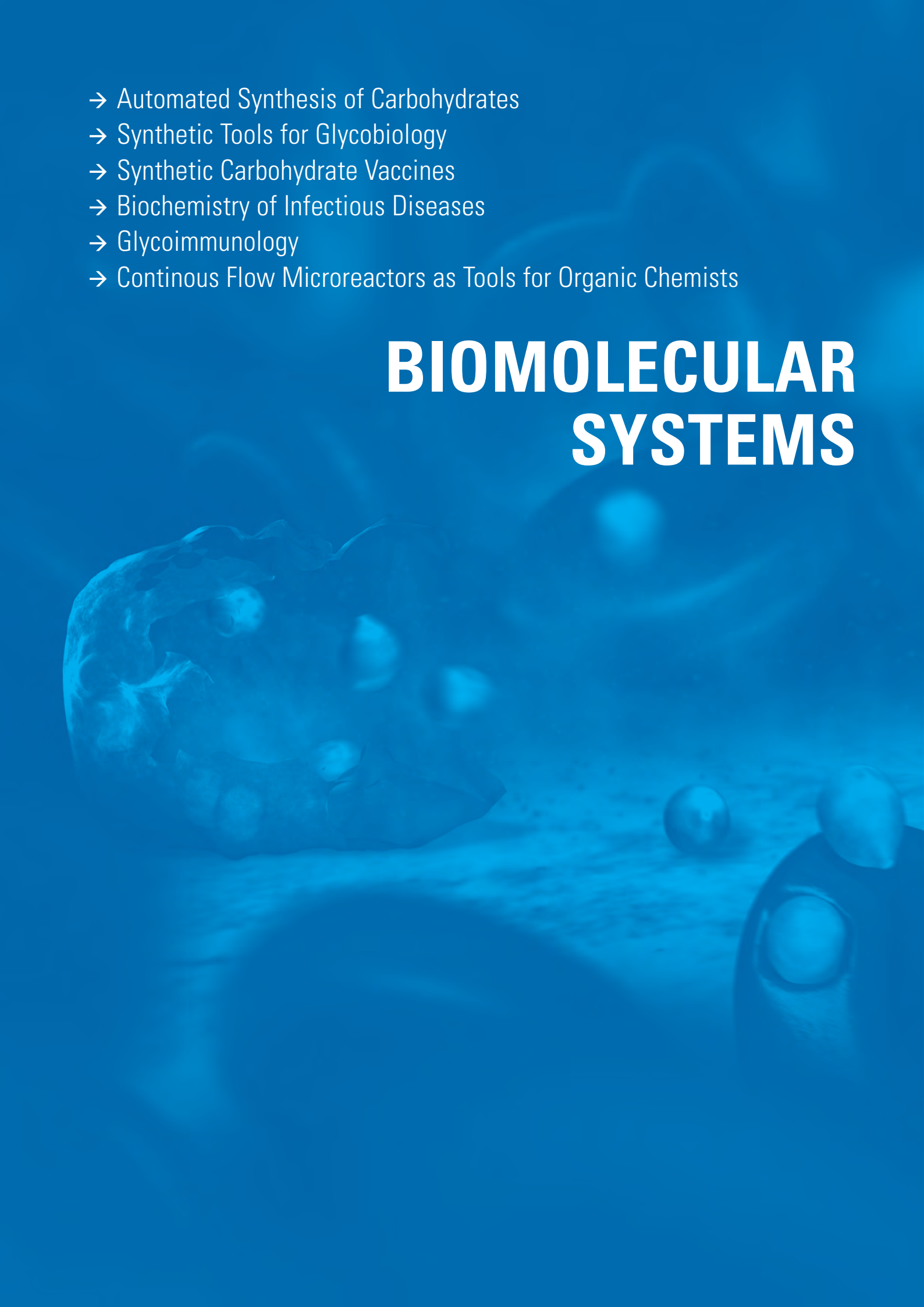
- → Automated Synthesis of Carbohydrates
- → Synthetic Tools for Glycobiology
- → Synthetic Carbohydrate Vaccines
- → Biochemistry of Infectious Diseases
- → Glycoimmunology
- → Continous Flow Microreactors as Tools for Organic Chemists

BIOMOLECULAR SYSTEMS



Research in the Department of Biomolecular Systems

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The Department of Biomolecular Systems, founded in 2009, conducts research at the **interface of chemistry, engineering, biology, immunology and medicine**. The core focus is the development of **synthetic methods** for the chemical synthesis of defined oligosaccharides. The compounds are the basis for **chemical tools** that aided **biochemical investigations** into the fundamental roles complex carbohydrates play in biological processes that underlie disease. The findings helped create diagnostic carbohydrate arrays to begin to understand **immunological aspects** of malaria epidemiology. **Vaccine development** of several infectious disease carbohydrate vaccine candidates is becoming increasingly more important for the laboratory. We are actively pursuing different aspects of glycobiology including the structure, function and biological role of sugars found on the surface of mammalian and bacterial cells particularly in the areas of immunology, biochemistry and human disease. Other areas of interest include ways to automate chemical synthesis and novel means to conduct chemical reactions using continuous-flow microreactors. Vaccine programs against infectious diseases including malaria, leishmaniasis, as well as a host of bacterial infections are currently progressing from synthesis to the preclinical stage.

Three major classes of polymers are responsible for the storage of information and signal transduction processes in biological systems. Nucleic acids make up the genetic material that transfers information from generation to generation. Proteins constitute the catalytic machinery carrying out most of the reactions in the cell. Carbohydrates, the third class of biopolymers, are branched, most complex and diverse. Access to pure carbohydrates was exceptionally difficult and therefore, all aspects of glycomics are less well understood than genomics and proteomics. A general, straightforward method for the procurement of oligosaccharides was needed to jump-start glycobiology the way molecular biology was impacted by the automated methods for DNA and peptide synthesis.

Automated Synthesis of Carbohydrates

The Department of Biomolecular Systems developed prior to the arrival in Potsdam, by solving a host of chemical problems, the **first automated oligosaccharide synthesizer [1]** as a platform to pursue glycomics as the next frontier in biology and medicine. This instrument provides now **access to many complex carbohydrates in days rather than years [2]**. Prototype instruments have been built to achieve these syntheses in a fully automated manner. This platform is currently being expanded to all classes of carbohydrates including glycolipids, glycoproteins, and heparin. All aspects of automated synthesis are being improved as novel methods resulted in excellent efficiency, selectivity and versatility of the synthetic process. The Department is closing in on the ultimate goal of creating a commercially available instrument that uses a defined set of monosaccharide building blocks to assemble most oligosaccharides reliably. Thus, non-specialists will be able to access defined sugars for biological or medical applications.

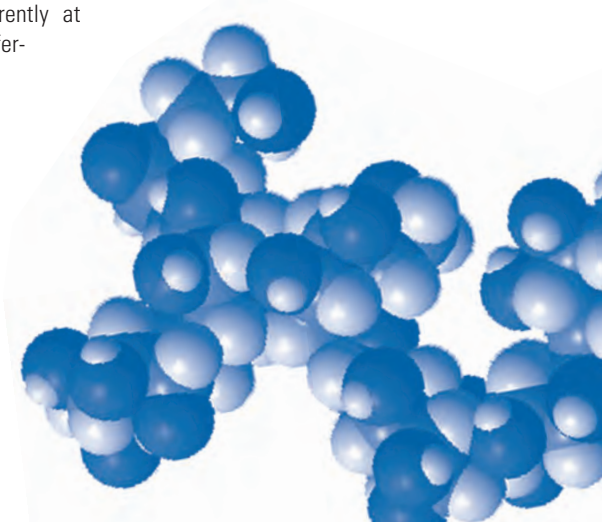
Synthetic Tools for Glycobiology

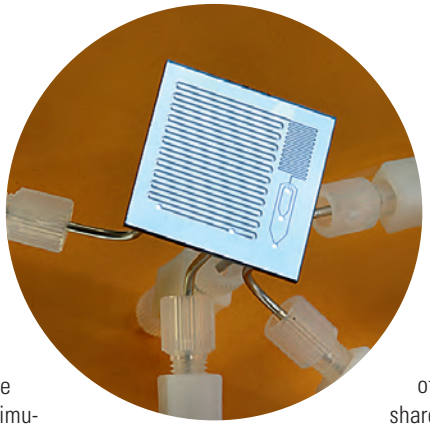
Rapid access to usable quantities of defined oligosaccharides has enabled the creation of **synthetic tools** that have been commonplace in genomics and proteomics research. These tools include **carbohydrate microarrays**, carbohydrate affinity columns to isolate carbohydrate-binding proteins and labeled carbohydrates for *in vitro* and in vivo imaging. The tools permitted us to explore fundamental aspects of glycobiology. The Seeberger group pioneered the use of carbohydrate microarrays to:

1) define HIV oligosaccharide antigens for the development of potential AIDS vaccines;
2) determine the ligands for carbohydrate-binding proteins;
3) understand the specificity and resistance problems of aminoglycoside antibiotics;
4) screen blood for disease patterns; and
5) **detect pathogenic bacteria in blood** and other body fluids. Particularly the ability to detect bacteria very sensitively in biological samples holds applications in food safety and the detection of blood poisoning. These more applied avenues are currently being expanded.

Synthetic Carbohydrate Vaccines

Based on the synthetic chemistry and tools platform, the Department has developed several applications. The presence of specific oligosaccharides on the surface of particular cell types including parasites, bacteria and cancer is the basis for the creation of synthetic carbohydrate vaccines against a host of diseases. An anti-toxin malaria vaccine candidate we identified **[8]** is currently in late preclinical development at a spin-off company and is expected to enter clinical trials in 2011. Carbohydrate arrays have provided the basis to demonstrate in epidemiological studies malaria resistance in endemic areas in Africa. It has been clearly shown that anti-toxin antibodies protect people in endemic areas after age two **[15]**! This finding strongly suggests that our vaccine candidate will provide protection for infants and naïve individuals much like that enjoyed by resistant individuals in endemic areas. Other vaccine candidates against infectious diseases are currently at differ-





ent stages of development: *anthrax* (animal tests), *leishmaniasis* (animal tests), tuberculosis (synthesis completed), avian flu (synthesis completed), and a host of bacterial diseases that are at different stages of development. Synthetic glycolipids have been found to be powerful immunostimulants for use as vaccine adjuvants.

Biochemistry of Infectious Diseases

The identification of the malaria toxin as a glycosylphosphatidyl inositol (GPI) anchor provided the basis for more detailed biological studies into the role of these complex molecules. In this context the department has been able to identify new signaling and entry mechanisms that are of crucial importance in malaria pathogenesis. These studies have provided the basis for different modes of intervention to fight this devastating protozoan parasitic disease.

Synthetically derived GPIs aid the quest to understand the role of **glycolipid signaling** in the inflammatory cascade, insulin independent signaling in diabetes and nerve growth. The past year has seen breakthroughs in the assembly of complete GPI-anchored prion proteins, an area that is now rapidly expanding. Biological investigations aiming at understanding **prion infectivity** in vivo are currently being initiated.

With the development of powerful synthetic tools in the department to generate carbohydrates the situation is increasingly changing leading to a better design of carbohydrate-based drugs and vaccines. A research group focuses on the development of peptide mimotopes of carbohydrates for vaccine development and to inhibit lectin-glycan interactions. Structural characterisation of peptide mimotopes of carbohydrates has provided important insights into the molecular mechanism of mimicry. Based on this information we will design phage-display libraries to improve the binding affinity of peptide mimotopes.

Glycoimmunology

The immunology group investigates the role of C-type lectin receptors (CLRs) in infections and autoimmune diseases. CLRs are carbohydrate-binding proteins of the innate immune system that share a conserved calcium-dependent carbohydrate recognition domain and include many endocytic receptors, collectins and selectins. CLRs belong to the innate immunity since they recognize conserved carbohydrate structures on pathogens and thus play a crucial role in the initiation of a protective immune response and for the maintenance of tolerance to autoantigens.

Animal models to analyze the function of CLRs during malaria infection and in autoimmune diseases such as colitis and encephalomyelitis have been established. The goal is to provide answers to the following questions: How is the expression pattern of CLRs altered during the course of infections and autoimmune diseases? Are CLRs involved in the induction of pathology during infection/inflammation? Do CLRs represent valuable drug targets to modulate ongoing immune responses *in vivo*?

Continous Flow Microreactors as Tools for Organic Chemists

Traditionally, organic chemists have performed chemical transformations in batch mode. Our department has pioneered the use of continuous flow microreactors for use by synthetic organic chemists. The department has utilized commercially available as well as internally developed microreactor systems to develop an automated reaction screening platform for organic chemists. Using these microreactor systems a host of chemical transformations has been rendered more efficient. In particular, dangerous, highly exothermic reactions as well as radical chemistry and photochemistry have benefited from the new way to run synthetic organic chemistry. Currently, these systems are being expanded to a host of applications in the area of total synthesis, methods development but most importantly, also to the preparation of organic and inorganic nanoparticles and colloids.

Prof. Peter H. Seeberger
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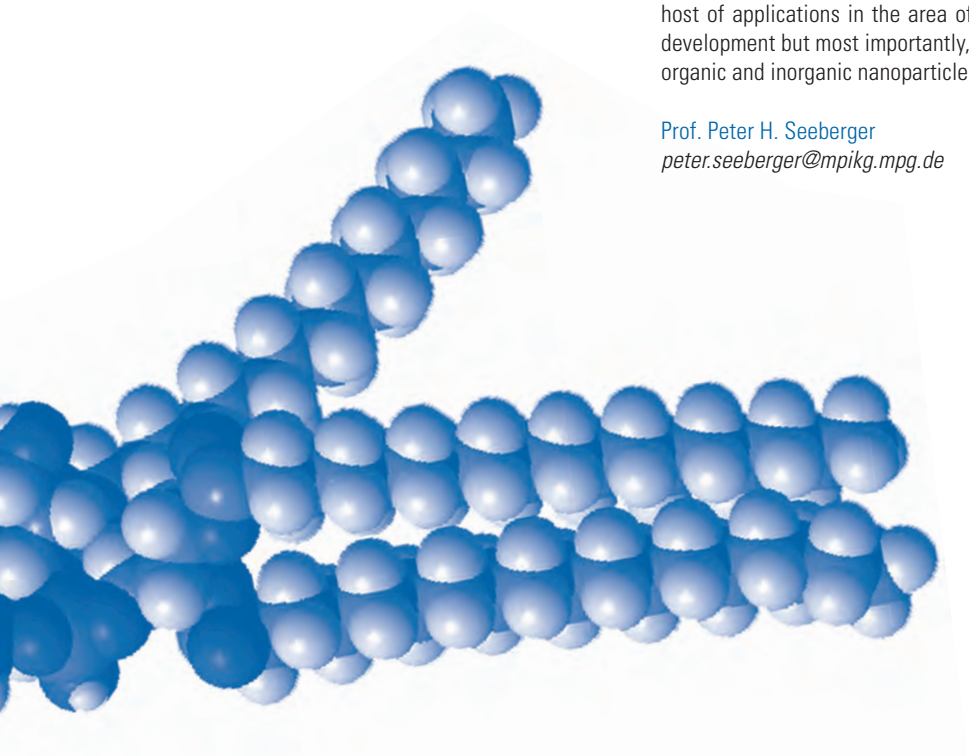

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*

APPENDIX

Organigramm
Organization Chart

Biomaterials
Director: Prof. Peter Fratzl · Secretary: Kerstin Gabbe

Biological Materials
- Hierarchical Connective Tissues/Dr. Himadri S. Gupta (Until 2008)
  Since October 2008 Lecturer in Biomaterials in the School of Engineering and Materials Science, Queen Mary University of London (UK)
- Bone Regeneration/Dr. Inderchand Manjubala
- Mechanobiology/Dr. Richard Weinkamer
- Biomimetic Actuation and Tissue Growth/Dr. John Dunlop (from 2009)
- Plant Biomechanics and Biomimetics/Dr. Ingo Burgert
- Bone Material Quality and Osteoporosis/Prof. Peter Fratzl, Dr. Admir Mašić,

Biological and Biomimetic Materials
- Biological and Bio-Inspired Materials/Prof. Peter Fratzl, Dr. Notburga Gierlinger, Dr. Matt Harrington, Dr. Paul Zaslansky
- Molecular Biomimetics and Magnet Biomineralization/Dr. Damien Faivre

Bioinspired Materials
- Biogenic Minerals and Bio-Inspired Nano-Composites/Dr. Barbara Aichmayer
- Mesoscale Materials and Synchrotron Research/Dr. Oskar Paris
  Since February 2009 Professor (W3) for Physics at the Montanuniversität Leoben (Austria)

Colloid Chemistry
Director: Prof. Markus Antonietti · Secretary: Annette Pape

Heterophase Polymerization
- Heterophase Polymerizations/Dr. Klaus Tauer

Self-organizing Polymers
- Bioinspirierte Polymere und Blockcopolymere/Dr. Helmut Schlaad
- Bioorganic-synthetic Hybridpolymers as molecularLEGO®-Bricks/Dr. Hans G. Börner
- Biomimetic Mineralization/Dr. Helmut Cölfen

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- Functional Carbonaceous and Polymeric Materials as Energy Sources and Stationary Phases for Separation Science/Dr. Maria-Magdalena Titirici
- De Novo Nanoparticles : Novel synthetic routes for nanoparticle production/Dr. Christina Giordano

Modern Techniques of Colloid Analysis
- Fractionating Colloid Analytics/Dr. Helmut Cölfen
- Electron Microscopic Studies of Colloidal Systems and Biomaterials/Dr. Jürgen Hartmann

MPI-FZU International Joint Laboratory
- MPI-FZU International Joint Laboratory/Dr. Xinchen Wang

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- Dilational Rheology of Mixed Protein-Surfactant Adsorption Layers/Dr. Reinhard Miller
- Thin Soft Films/Dr. Rumen Krastev
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- Ion Distribution at Interfaces/Dr. Hubert Motschmann
  Since October 2008 Professor (W2) forPhysical Chemistry at the University Regensburg

Solid Interfaces
- Nucleation, Interfacial Molecular Mobility and Ordering of Alkanes at Solid/Vapor Interfaces/Dr. Hans Riegler

Non-Planar Interfaces
- From Molecular Modules to Modular Materials/Dr. Dirk G. Kurth
  Since October 2008 Professor (W2) for Chemical Technology of Material Synthesis at the University Würzburg
- Active Coatings Based on Incorporated Nanocontainers/Dr. Dmitry Shchukin
- Functional Multilayers and Capsules/Prof. Helmuth Möhwald, Dr. Andre Skirtach
- Ordering of Functional Nanoparticles/Dr. Dayang Wang

International Joint Laboratories
- Supramolecular Nanomaterials/Dr. Takashi Nakanishi
- Molecular Assemblies of Biomimetic Systems and Nanostructures/Prof. Junbai Li
- Laboratoire Européen Associé (LEA) on Sonochemistry/Dr. Dmitry Shchukin, Prof. Helmuth Möhwald

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- Semiflexible Rods and Filaments/Dr. Jan Kierfeld
  Since October 2007 Professor (W2) for Theoretical Physics at the Technical University Dortmund
- Phase Behavior of Rigid Rods/Dr. Thomas Gruhn
  Since January 2008 Research Assistant at the Institute of Anorganic and Analytic Chemistry at the University Mainz

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Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
BMBF	Bionik (2): Übertragung des Konzepts der Matrixeinbettung von Pflanzenfasern auf technische Faserverbundwerkstoffe	Dr. Burgert BM	01.07.2006-31.03.2007	Institut für Textil- und Verfahrens-technik Denkendorf, Botanischer Garten der Universität Freiburg
BMBF	Bionik (2): Faserverbundwerkstoffe mit graduellen Matrixübergängen; Teilprojekt 1	Dr. Burgert BM	01.05.2008-40.04.2011	Albert-Ludwigs-Universität Freiburg, Universität Bayreuth
BMBF	Max-Planck-Forschungspreis 2008: Biological and Biomimetic Materials	Prof. Fratzl BM	01.09.2008-31.12.2013	
BMBF	Experimentelle und theoretische Untersuchungen zur Bildung und Deformation von Einzeltropfen Modell für Schäume und Emulsionen	Dr. Miller GF	01.01.2007-30.06.2009	
BMBF	Nanoskalige Hohlstrukturen mit eingebetteten Gastmolekulen für neue aktive Korrosionsschutz-Systeme	Dr. Shchukin GF	01.05.2007-30.04.2011	Capsulution NanoScience AG Berlin; PlasmaChem GmbH, Berlin; EADS Deutschland GmbH, München; BASF Coatings GmbH, Münster
BMBF	Planare Nanostrukturen an festen Oberflächen	Prof. Vollhardt GF	01.07.2007-31.12.2009	National Academy of Sciences of Ukraine
BMBF	SOHyb: Keimbildungsinduzierte Selbstorganisation zur Strukturierung organischer Hybridsolarzellen	Dr. Riegler GF	01.11.2008-30.04.2012	Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Chemtec Leuna, Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam Justus-Liebig-Universität, Gießen
EU				
EU	Cellulose Architecture Systems Biology for Plant Innovation Creation	Prof. Fratzl Dr. Burgert BM	01.01.2007-31.12.2009	Wageningen Universiteit, Niederlande; Stiching voor Fundamenteel Onderzoek der Materie, Niederlande; Sveriges Lantbruksuniversitet, Uppsala; Institut National de Recherche Agronomique, Paris SweTree AB, Schweden
EU	Nanocapsules for Targeted Controlled Delivery of Chemicals	Dr. 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

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GF – Abteilung Grenzflächen/Department of Interfaces
KC – Abteilung Kolloidchemie/Department of Colloid Chemistry
TH – Abteilung Theorie & Bio-Systeme/Department of Theory & Bio-Systems

EU

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
EU	Nanoengineered Chemical Synthesis Inside Restricted Volume of Nano- and Microsized Polyelectrolyte Capsules	Prof. Möhwald Dr. Sukhorukov GF	01.05.2005-30.04.2007	
EU	Development of Multifunctional Nanometallic Particles using a new Process-Sonoelectrochemistry	Prof. Möhwald Dr. Sukhorukov GF	01.03.2005-31.12.2007	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	System for In-Situ Theranostic Using Microparticles Triggered by Ultrasound	Dr. Fery GF	01.10.2006-31.05.2007	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 Capsulation 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
EU	Bioimaging with Smart Functional Nanoparticles	Prof. Möhwald Dr. Wang GF	01.11.2006-31.10.2009	ENEA, Rom; Commissariat a l´energie atomique, Paris Consejo Superior de Investigaciones Cientificas, Madrid; Universidad Complutense de Madrid Universita delgi Studi die Padova Universita die Milana-Bicocca, Italien; Guerbet, Frankreich Russian Academy Institute of General Physics, Russian Academy of Science; Albert-Ludwigs-Universität Freiburg; Nanovector srl, Italien; TILL Photonics GmbH, Gräfelfing

EU

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
EU	Development of a New Biocoating-Multilayered Polyelectrolyte Film with Incorporated Drug-Loaded Liposomes	Prof. Möhwald GF	01.10.2007-30.09.2009	
EU	Open Tok: Development of Smart Polymer Surfaces	Prof. Möhwald GF	01.01.2007-31.12.2009	University of Maribor, Slovenien
EU	Novel Nanocomposites for Hydrogen Storage Applications	Prof. Möhwald Dr. Shchukin GF	01.01.2008-30.09.2011	Forschungszentrum Karlsruhe Consiglio Nazionale delle Ricerche, Rom; CNRS, Paris FutureCarbon GmbH, Bayreuth Institutt for energiteknikk, Norwegen; National Center for Scientific Research "Demokritos", Griechenland; Universität Oslo
EU	Multi-Level Protection of Materials for Vehicles by "Smart" Nanocontainers	Prof. Möhwald Dr. Shchukin GF	01.06.2008-31.05.2012	EADS Deutschland GmbH Universidade de Aveiro, Portugal Stiftelsen Sintef, Norwegen Universität Paderborn; Mankiewic Gebr.&Co. GmbH & Co KG, Hamburg Bayer Technology Services GmbH, Leverkusen; National Center for Scientific Research "Demokritos", Griechenland; Sika Technology AG, Schweiz; Instytut Katalizy i fizyko-chemii Powierzchni, Polska Akademia Nauk, Krakau Steinbeis Advanced Risk Techno-logies GmbH, Stuttgart; Instituto Superior Tecnico, Lissabon Centro Richerche Fiat SCPA, Italien RE-TURN AS, Norwegen Varnish SRL, Italien; Daimler AG, Stuttgart; Chemetall GmbH, Frankfurt/M.; Helsingin Yliopisto, Finnland; European Virtual Institute on Knowledge-based Multi-functional Materials AISBL, Belgien
EU	Self-Organized Nanostructures of Amphiphilic Copolymers	Prof. Antonietti KC	01.01.2004-28.02.2007	TU 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	Hydrothermal and Ionothermal Chemistry for Sustainable Materials	Prof. Antonietti KC	01.11.2008-31.10.2013	
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

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
EU	Active Biomimetic Systems	Prof. Lipowsky Dr. Valleriani TH	01.05.2005-30.10.2008	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

DFG

DFG	Mesoskopisch strukturierte Verbundsysteme; Wandverformung bei Mesoporen bei der Kappilarkondensation von Fluiden	Prof. Fratzl Dr. Paris BM	01.01.2007-	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam
DFG	DFG Graduate School 203: Berlin-Brandenburg School for Regenerative Therapies	Prof. Fratzl BM	01.11.2007 - 31.10.2012	Charité - Universitätsmedizin Berlin Freie Universität Berlin GKSS Research Center Humboldt-Universität zu Berlin Max-Planck-Institute for Molecular Genetics Technische Universität Berlin Universität Potsdam Zuse Institute Berlin
DFG	Biomechanics and Biology of Musculosketal Regeneration-From Functional Assessment to Guided Tissue Formation; The Micro-Mechanical and Structural Properties of Callus Tissue During Bone Healing	Prof. Fratzl Dr. Manjubala BM	01.01.2007-	Charité - Universitätsmedizin Berlin Freie Universität Berlin Max-Planck-Institut für molekulare Genetik; Deutsches Rheuma-Forschungszentrum Berlin Helmholtz-Gemeinschaft Deutscher Forschungszentren; Institut für Polymerforschung; GKSS-Forschungszentrums Geesthacht GmbH, Teltow; Zuse Institut Berlin
DFG	Biomechanics and Biology of Musculosketal Regeneration – From Functional Assessment to Guided Tissue Formation; Mechano-Biology of Bone Healing and Regeneration	Dr. Weinkamer BM	01.01.2007-	Charité - Universitätsmedizin Berlin Freie Universität Berlin Max-Planck-Institut für molekulare Genetik; Deutsches Rheuma-Forschungszentrum Berlin Helmholtz-Gemeinschaft Deutscher Forschungszentren; Institut für Polymerforschung; GKSS-Forschungszentrums Geesthacht GmbH, Teltow; Zuse Institut Berlin
DFG	Biomechanics and Biology of Musculosketal Regeneration – From Functional Assessment to Guided Tissue Formation;Regulation of the Biosynthesis of Extracellular Matrix Components by Biomaterial Scaffolds of Different Geometry and Stiffness	Prof. Fratzl BM	01.01.2007-	Charité - Universitätsmedizin Berlin Freie Universität Berlin Max-Planck-Institut für molekulare Genetik; Deutsches Rheuma-Forschungszentrum Berlin Helmholtz-Gemeinschaft Deutscher Forschungszentren; Institut für Polymerforschung; GKSS-Forschungszentrums Geesthacht GmbH, Teltow; Zuse Institut Berlin

DFG

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Mesoskopisch strukturierte Verbundsysteme; Hierarchische Architekturen aus Modulen mit metallosupramolekularen Koordinations-Polyelektrolyten	Prof. Möhwald Dr. Kurth GF	01.01.2001-	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam
DFG	Mesoskopisch strukturierte Verbundsysteme; Ordnungsstrukturen in Systemen aus stäbchen-förmigen Molekülen	Prof. Lipowsky TH	01.01.2004-	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam
DFG	Mesoskopisch strukturierte Verbundsysteme; Molekulare Prozesse in mesoskopisch struk-turierten Polyelektrolytsystemen	Prof. Möhwald GF	01.01.2004-	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam
DFG	Generation of Anisotropic Hydrogel Membranes, Mimicking Plant Cell Wall Structures, and Exploration of New Bio-Inspired Mechanical Devices Based on Gel Swelling	Dr. Burgert BM	01.01.2008-	
DFG	Dynamics of Interfaces between Drops with Miscible Liquids	Dr. Riegler GF	01.09.2008-	
DFG	Counterion Distribution in Aligned Lamellar Phases and on Monlayers at the Air/Water Interface	Prof. Möhwald GF	01.11.2004-30.11.2007	
DFG	Molecular Magnetism of Metallo-Supromolecular, Hierarchically Ordered Materials Containing Periodically Arranged Metal-Ligand-Complexes	Dr. Kurth GF	01.06.2005-30.06.2008	
DFG	Structure-Mechanical Property Relations of Poly-electrolyte Multilayer and Free-Standing Membranes	Dr. Fery GF	01.05.2006-03.02.2008	
DFG	Remote (Microwave) Activated Release from Composite Nanoparticle/Polymer Microcapsules (Deutsch-Russisches Kooperationsprojekt)	Prof. Möhwald GF	17.10.2006-14.04.2008	
DFG	Generation of Anisotropic Hydrogel Membranes, Mimicking Plant Cell Wall Structures, and Exploration of New Bio-Inspired Mechanical Devices Based on Gel Swelling	Dr. Wang GF	01.12.2007-	
DFG	Generation of Anisotropic Hydrogel Membranes, Mimicking Plant Cell Wall Structures, and Exploration of New Bio-Inspired Mechanical Devices Based on Gel Swelling	Dr. Krastev GF	30.04.2008-	
DFG	Zusammenarbeit mit Ägypten: Förderung des Gastaufenthaltes von Dr. M. Ryad Noor El-Din	Dr. Miller GF	03.05.2008-02.07.2008	

DFG

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Intelligent Release Systems for Anticorrosion Self-Healing Coatings (Deutsch-Russisches Kooperationsprojekt)	Prof. Möhwald GF	17.07.2008-16.07.2011	
DFG	Structural and Morphological Characterization of Ceramide-1-Phoshate Model Membran	Dr. Brezesinski GF	01.09.2008-	
DFG	Charakterisierung von Grenzflächen zwischen zwei Flüssigkeiten unter hoch-dynamischen Bedingungen	Dr. Miller GF	01.08.2007-31.07.2009	
DFG	Complex Fluids: From 3 to 2 Dimensions (Deutsch-Französisches Netzwerk)	Prof. Möhwald GF	01.01.2003-31.12.2007	
DFG	Exzellenzcluster UniCat: Unifying Concepts in Catalysis	Prof. Antonietti KC Prof. Möhwald GF	01.01.2008-31.12.2010	Technische Universität Berlin Humboldt-Universität Berlin Freie Universität Berlin; Universität Potsdam; Fritz-Haber-Institut der Max-Planck-Gesellschaft Berlin
DFG	Emmy-Noether-Programm: Bioorganische und biomimetische Polymere zur programmierbaren Strukturierung synthetischer Polymermaterialien: Synthese, Charakterisierung und Anwendung der Polymerhybridsysteme	Dr. Börner KC	01.04.2005-31.03.2009	
DFG	Synthese von Nanodrähten und Nanoröhren druch kontrollierte Organisaion oberflächenfunktional-isierter Metalloxid-Nanopartikel	Dr. Niederberger KC	15.07.2004-14.04.2007	
DFG	Materials World Network to Study Liquid PrecursorFormation and Crystallization at Interfaces: Fundamentals Towards Applications	Dr. Cölfen KC	01.01.2008-	
DFG	Higher Levels of Self-Assembly of Ionic Amphiphilic Colpolymers (SONS-AMPHI)	Dr. Schlaad KC	01.10.2003-31.01.2007	
DFG	SONS-Biofunctional Self-Organized Nano-Structures of Ionic/Non-Ionic Amphiphilic Copolymer, Biopolymer-Biomacromolecules and Nanoparticles: From Bioinspired to Biointegrated Systems	Dr. Schlaad KC	01.01.2007-	
DFG	Spektroskopische ellipsometrische Lichtstreuung an Flüssigkristall-Miniemulsionen	Dr. Sigel KC	01.01.2005-31.08.2007	
DFG	Retrosynthese von Biomineralien über mesoskop-ische Transformation von amorphen Precurso-partikeln in natürlichen organischen Matrizen	Dr. Cölfen KC	01.01.2006-15.08.2007	
DFG	Structure Elucidation of Shear Oriented Ionic Self-Assembled Materials (SISAM)	Prof. Antonietti KC	09.09.2003-14.02.2007	
DFG	Controlled Precipitation of Biominerals Using Catanionic Surfactant Self-Assembly Structures	Dr. Cölfen KC	15.08.2004-30.04.2008	
DFG	Adhäsion und Fusion von Lipid-Membranen	Dr. Dimova TH	01.01.2004-14.03.2007	

Unteraufträge/Weiterleitungen and deutsche Forschungseinrichtungen

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
Universität des Saarlandes	Neuartige Carrier zur Inhalation von Wirkstoffen basierend auf der Layer-by-Layer Technologie	Prof. Möhwald GF	01.01.2008-31.12.2010	Boehringer Ingelheim International GmbH
LIKAT	Unterauftrag zum AIF-Projekt: Mesoporöse Hybridsysteme	Prof. Antonietti Dr. Smarsly KC	01.09.2006-31.07.2007	Leibniz-Institut für Katalyse, Rostock
Deutsche Bundesumwelt Stiftung	Hydrothermale Carbonisierung	Prof. Antonietti KC	01.04.2008-31.03.2009	Hochschule Ostwestfalen-Lippe
BMBF/ Universität Potsdam	GoForsys Potsdam-Golm BMBF-Forschungs-einrichtung zur Systembiologie. Photosynthesis and Growth: A Systems Biology based Approach	Prof. Lipowsky TH	01.01.2007-31.12.2011	Universität Potsdam MPI für molekulare Pflanzenphysiologie
Supranationale Einrichtungen				
ESA	Bone Structure, Changes in Microgravity	Dr. Saparin BM	01.03.2007-29.02.2008	Charité, Berlin; Universität Potsdam ZIB Berlin; Ludwig Boltzmann Institute of Osteology, Wien Scanco Medical AG; Siemens AG
ESA/ESTEC	Fundamental and Applied Studies of Emulsion Stability	Dr. Miller GF	01.10.2003-31.12.2009	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	01.10.2003-30.12.2008	CNR, Genua, Italien Universität Lorence, Italien Universität Marseille, Frankreich Universität Compienge, Frankreich IPF Dresden
NATO	Novel Feedback-Active Coatings based on Incorporated Nanocontainers	Dr. Shchukin GF	17.04.2007-03.07.2008	
HFSP	Polymerization of Actin filaments	Prof. Lipowsky TH	01.05.2005-31.03.2007	
Stiftungen				
AvH-Stiftung	Forschungskostenzuschüsse an Gastinstitute von Stipendiaten der AvH	Prof. Fratzl Prof. Lipowsky Prof. Antonietti Prof. Möhwald	01.01.2007-	
Minerva-Stiftung	German-Israeli-Minerva-School 2007	Dr. Zaslansky BM	01.05.2007-30.06.2007	Weizmann Institute of Science, Israel; Ben Gurion University, Israel
Körber-Stiftung	Körber-Preis 2007	Prof. Seeberger BS	01.01.09.2007-	

Stiftungen

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
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	Formation of Bi-Functional Coatings on Metals based on Self-Locating Nano- and Microcontainers	Dr. Shchukin GF	01.08.2008-31.07.2011	Universität Paderborn Fraunhofer Institut für Schicht- und Oberflächentechnik
VW-Stiftung	Blockcopolymer Vesicles with Controlled Uptake/Release Functions for Drugs and Gen	Prof. Antonietti KC	15.07.2004-14.07.2007	Uni Hamburg Universität Duisburg Universität Freiburg

Ausländische Forschungsfinanzierer

FWF Wien	Charakterisierung unbehandelter und modifizierter Holzfasern	Dr. Burgert BM	01.11.2003-30.09.2007	
National Institute of Health (USA)	Matrix Protein Regulation of Enamel Mineral Formation	Prof. Fratzl BM	01.08.2005-31.07.2009	
GIF	Understanding the Toughness of Biological Mineralised Tissues	Prof. Fratzl BM	01.01.2005-31.12.2007	Weizmann Institute of Science, Rehovot
Japan Science and Technology Agency	Development of Novel Materials Employing Supramolecular Fullerenes with Controlled Dimensionality	Prof. Möhwald Dr. Nakanishi GF	01.04.2007-31.03.2010	
NCSU	Single-Step Portein Surface-Attachment to Electrospun Fibers	Dr. Börner KC	01.05.2004-30.04.2007	

Industrie

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
BASF Coatings	Nanoskalige Hohlstrukturen mit eingebetteten Gastmolekülen	Prof. Möhwald Dr. Shchukin GF	01.02.2007-	
Bayer Vital GmbH	Mechanism of Actioin of Simethicone/Dimethicone as a Defoaming/Antifoaming Agent	Dr. Krastev GF	01.02.2008-31.07.2008	
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 Capilar Systems for Nano-LC	Prof. Antonietti Dr. Smarsly KC	01.03.2004-31.10.2008	
BASF	Mesoporöse Hybridsysteme	Prof. Antonietti Dr. Smarsly KC	01.05.2006-30.04.2007	

Industrie

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
Merck	Entwicklung mobiler Gasspeicher auf der Basis nanoporöser Kohlenstoffmaterialien	Prof. Antonietti KC	01.09.2007-31.08.2008	
Merck	Entwicklung neuartiger Elektrodenmaterialien auf der Basis von nanoporösen Kohlenstoffmaterialien zur Anwendung in elektochemischen Speichern	Prof. Antonietti KC	01.08.2007-31.07.2009	
BASF	Synthese und Verwendung von Carbonnitrid	Prof. Antonietti KC	15.10.2007-31.12.2010	
BASF	Carbon Rich Polymer Colloids for Applications for Architectural Coatings, Adhesives, Fibre Bonding, Construction Chemicals and Paper Chemicals	Prof. Antonietti KC	01.01.2008-30.06.2010	
Bayer Schering Pharma	Nanotechnologie für das molekular-bildgeführte Gesundheitsmanagement (Eisenherz); Unterauftrag des BMBF: Synthese neuartiger Eisenoxidartikel mit kontrolliertem Verbleib	Prof. Antonietti KC	01.08.2005-31.07.2008	

Sonstige deutsche Forschungsfinanzierer

HMI Berlin GmbH	Wissenschaftliche und technische Zusammenarbeit auf dem Gebiet der Untersuchung von Oberflächen und dünnen Schichten mit Neutronenstreuung	Prof. Möhwald GF	01.01.1999-	
DAAD	Projektbezogener Austausch mit Portugal	Dr. Brezesinski GF	01.01.2006-31.12.2007	
DAAD	Projektbezogener Austausch mit Portugal	Dr. Shchukin GF	01.01.2007-31.12.2008	
DAAD	Projektbezogener Austausch mit Bulgarien	Dr. Miller GF	01.01.2005-31.12.2008	
DAAD	Projektbezogener Austausch mit Spanien	Dr. Miller GF	01.01.2007-31.12.2008	
DAAD	Projektbezogener Austausch mit Frankreich	Dr. Shchukin GF	01.01.2008-31.12.2009	
DAAD	Projektbezogener Austausch mit Griechenland	Dr. Sigel KC	01.01.2006-31.12.2007	

Ausgewählte Veranstaltungen
Selected Events

- **25. March 2007 „Potsdamer Köpfe", Sunday Lectures in Potsdam**
  Prof. Peter Fratzl: Wenn der Knochen bricht – Materialforscher für die Medizin (Altes Rathaus Potsdam)

- **24. May 2007 Kick-Off Colloquium**
  Campus Project "Bioactive Surfaces" (Research Campus Potsdam-Golm)

- **29. May - 2. June 2007 Minerva School on Biological and Bioinspired Materials together with Minerva Students' Symposium 2007**
  (Harnack-Haus, Berlin)

- **8. June 2007 Alumni Meeting and Poster Session**
  Research Campus Potsdam-Golm

- **19. July 2007 SommerMINTCollege**
  Research Campus Potsdam-Golm

- **1. September 2007 Open Day at the Research Campus Potsdam-Golm**
  Research Campus Potsdam-Golm, Campus Am Mühlenberg

- **19. October 2007 HerbstMINTCollege**
  Research Campus Potsdam-Golm

- **26.-27. November 2007 Meeting of the Scientific Advisory Board**
  Research Campus Potsdam-Golm

- **13. March 2008 1. Schüler-Campus Brandenburg**
  Research Campus Potsdam-Golm

- **11.-14. March 2008 COST D43 - School on Surface Analytical Techniques**
  Research Campus Potsdam-Golm

- **11. April 2008 ENERCHEM Evaluation**
  Harnack-Haus, Berlin

- **16. April 2008 38. Meeting of the Committee of Science, Research and Culture of the Landtag of Brandenburg together with the Committee of Science and Research of the House of Deputies, Berlin**
  Research Campus Potsdam-Golm

- **9. May 2008 1st Golm Workshop on Bioactive Surfaces**
  Research Campus Potsdam-Golm

- **23. May 2008 Alumni Meeting and Poster Session**

- **24. July 2008 SommerMINTCollege**
  Research Campus Potsdam-Golm

- **28. July 2008 Delegations visit of the Royal Thai Embassy in cooperation with the Nanonet of Thailand**
  (Research Campus Potsdam-Golm)

- **17.-22. August 2008 17th SIS 2008 - 17th International Symposium on Surfactants in Solution**
  Berlin, Germany

- **6. September 2008 Open Day at the Research Campus Potsdam-Golm**
  Research Campus Potsdam-Golm, Campus University Potsdam

- **6. November 2008 Constitutive Meeting of the Board of Trustees**
  MPI of Molecular Plant Physiology, MPI of Colloids and Interfaces)

Wissenschaftliche Abschlüsse
Scientific Degrees

Diploma Theses

Department of Biomaterials:

Lange, Claudia: Quantitative und qualitative Analyse der Gewebeentstehung in vitro. Universität Potsdam (2007).

Kerschnitzki, Michael: Die Kontrolle der mechanischen Eigenschaften von Knochen durch die Veränderung der Temperatur, der Dehnrate, des pH-Wertes und des ionischen Mediums. Universität Potsdam (2008).

Department of Interfaces:

Christiane, Stage: Synthesen, Charakterisierung und Eigenschaften von supramolekularen Systemen. Universität Potsdam (2008).

Master Theses

Department of Interfaces:

Bai, Shu: Loading Hydrogel Microspheres with Inorganic Nanoparticles. Polymer Science Program: Free University Berlin, Humboldt University, Technical University, University Potsdam (2007).

Department of Colloid Chemistry:

Su, Qi: Synthesis of PBIs with Different Architectures (Master of Polymer Sciences), Free University Berlin, Technical University, University Potsdam (2007).

Yu. Yingchuan: Free Radical Polymerization on Crystal Templates (Master of Polymer Sciences, Free University Berlin, Technical University, University Potsdam (2007).

PhD Theses

Department of Biomaterials:

Eder, Michaela: Structure, Properties and Function of Single Wood Fibres of Norway Spruce. Universität für Bodenkultur in Wien (2007).

Ruffoni, Davide: Modeling of Material and Architectural Quality of Trabecular Bone. Universität Potsdam (2007).

Sapei, Lanny: Characterisation of Silica in Equisetum hyemale and its Transformation into Biomorphous Ceramics. Universität Potsdam (2007).

Jungnikl, Karin: The Macromolecular Structure of Wood Cell Walls and its Significance for Selected Hierarchical Levels. Universität Freiburg im Breisgau (2008).

Department of Colloid Chemistry:

Adelhelm, Philipp: Novel Carbon Materials with Hierarchical Porosity: Templating Strategies and Advanced Characteriaztion. Universität Potsdam (2007).

Hartmann, Laura: Synthese monodisperser, multifunktionaler Poly(amidoamine) und ihre Anwendung als nicht-virale Vektoren für die Gentherapie. Universität Potsdam (2007).

Kaper, Helena: Structure Control of Nanoscaled Inorganic Matter by Ionic Liquids. Universität Potsdam (2007).

Sel, Özlem: Hierarchical Meso- and Macroporous Architectures by Liquid Crystalline and Polymer Colloid Templating. Universität Potsdam (2007).

Stocco, Antonio: Amphiphilic Block Copolymers at the Liquid-Fluid Interface, Investigated by Evanescent Light Scattering and Ellipsometry. Universität Potsdam (2007).

Weber, Jens: Meso- und Mikroporöse Hochleistungspolymere – Synthese, Analytik und Anwendung. Universität Potsdam (2007).

You, Liangchen: Synthesis and Characterization of Novel Glycopolymers. Universität Potsdam (2007).

Buha, Jelena: Nonaqueous Synthesis of Metal Oxide and Metal Nitride Nanoparticles. Universität Potsdam (2008).

Fischer, Anna: "Reactive Hard Templating" From Carbon Nitrides to Metal Nitrides. Universität Potsdam (2008).

Greß, Anja: Funktionalisierte Poly(2-oxazoline): Kontrollierte Synthese, bioinspirierte Strukturbildung und Anwendungen. Universität Potsdam (2008).

Gebauer, Denis: A Novel View on the Early Stage of Crystallization. Universität Potsdam (2008).

Hentschel, Jens: Synthese und kontrollierte Mikrostrukturbildung funktionaler Peptid-Polymer-Konjugate in organischen Lösungsmitteln. Universität Potsdam (2008).

Hernàndez Garcia, Hugo: Multicscale Simulation of Heterophase Polymerization: Application to Synth. of Mulitcomponent Colloidal Polymer Particles. Universität Potsdam (2008).

Hordyjewicz-Baran, Zofia: Synthesis and Study of the Aggregation Behavior of Hydrophilically Modified Polybutadienes. Universität Potsdam (2008).

Ide, Andreas: Self-Structuring of Functionalized Micro- and Mesoporous Organosilicas using Boron-Silane-Precursors. Universität Potsdam (2008).

Kessel, Stefanie: Induktion und Kontrolle hierarchischer Ordnung durch selbstorganisierte, funktionale Polymer-Peptid-Nanostrukturen. Universität Potsdam (2008).

Maier, Julia: Synthese und Anwendungen von FERR-*b*-PEO stabilisierten *SPIO* Partikeln als Kontrastmittelsystem für die Magnetresonanztomographie. Universität Halle-Wittenberg (2008).

Nazaran, Pantea: Nucleation in Emulsion Polymerization - Steps towards a Non-micellar Nucleation Theory. Universität Potsdam (2008).

Stark, Arne: CCD based Ellipsometric Light Scattering. Universität Potsdam (2008).

Yagci, Yavuz Emre: Synthesis of Poly(tartar Amide)s and Poly(gluco amide)s as Antifreeze Additives. Universität Potsdam (2008).

Department of Interfaces:

Alahverdjieva, Veneta: Experimental Study of Mixed Protein/ Surfactant Systems at the Aqueous Solution/Air Interface. Universität Potsdam (2007).

Günther, Anja: Mikrokapseln aus biokompatiblen Polyelektrolytmultischichten als DNA- und Proteinvehikel. Universität Potsdam (2007).

Köhler, Karen: Temperature-Induced Rearrangements of Polyelectrolyte Multilayer Capsules: Mechanisms and Applications. Universität Potsdam (2007).

Müller, Renate: Einfluss der Temperatur auf die Nanomechanik von sphärischen und zylindrischen Polyelektrolyt-Multischicht-Hohlkörpern. Universität Potsdam (2007).

Wagner, Kerstin: The Regulation of Phospholipase Activity by Lipid Membrane Structure. Universität Potsdam (2007).

Borodina, Tatiana Nikolaevna: Preparation and Examination of Biodegradable Polyelectrolyte Microcapsules with Control Release of Proteins, DNA and other Bioactive Substance". Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences (2008).

Dronov, Roman: Assembly of Functional Biological Systems at Interfaces. Universität Potsdam (2008).

Hermelink, Antje: Phosphatidylinositole 3-kinase gamma: Biophysical Approach on a Protein-Lipid Interaction. Humboldt-Universität zu Berlin (2008).

Miyashita, Naoko: Molecular Assemblies on Surfaces. Universität Potsdam (2008).

Olak, Claudia: Biophysikalische Studien zur Wechselwirkung des antimikrobiellen Peptides NK-2 mit membran-mimetischen Systemen. Universität Potsdam (2008).

Schwarz, Guntram: Synthesen, Charakterisierung und Eigenschaften von supramolekularen Systemen. Universität Potsdam (2008).

Department of Theory and Bio-Systems:

Beeg, J.: Cooperative Behavior of Motor Proteins. Universität Potsdam (2007).

Chelakkot, G.R.: Structure in Systems of Chemically Heterogenous Rods. Universität Potsdam (2007).

Grafmüller, A.: The Fusion of Membranes and Vesicles. Universität Potsdam (2007).

Gutjahr, P.: Conformations of Semiflexible Polymers and Filaments. Universität Potsdam (2007).

Gutlederer, E.J.: On the Morphology of Vesicles. Universität Potsdam (2007).

Korn, C.: Stochastic Dynamics of Cell Adhesion in Hydrodynamic Flow. Universität Potsdam (2007).

Koseska, A.: Modeling and Control of Synthetic Gene Regulatory Networks. Universität Potsdam (2007).

Kühne, T.: Wachsende Filamentbündel. Universität Potsdam (2007).

Liepelt, S.: Energy Transduction in Network Models of Molecular Motors. Universität Potsdam (2007).

Merlo, C.: Ein einfaches Modell der Proteinfaltungskinetik. Universität Potsdam (2007).

Richter, A.: Structure Formation and Fractionation in Systems of Colloidal Rods. Universität Potsdam (2007).

Blecua, P.: Liquid Morphologies on Patterned Surfaces. Universität Potsdam (2008).

Chai, Y.: Traffic of Molecular Motors. Universität Potsdam (2008).

Müller, M.: Bidirectional Transport by Molecular Motors. Universität Potsdam (2008).

Schwenk, B.: Two Notions of Membrane Tension. Universität Potsdam (2008).

Habilitations

Department of Biomaterials:

Burgert, I.: On the Mechanical Design of Plant Cell Walls. Humboldt-Universität zu Berlin (2007).

Department of Theory and Bio-Systems:

Gruhn, T.: Biomimetic self-assembling structures: From Systems of Colloidal Rods to Fluid Vesicles. Technische Universität Berlin (2008).

Weikl, T.: Transition States and Loop-Closure Principles in Protein Folding. Universität Potsdam (2008).

Personalien
Appointments and Honors

2007
Ehrungen/Mitgliedschaften/Honorarprofessuren
Honors/Memberships/Honorary Professorships

Prof. Dr. Markus Antonietti	Director of the Colloid Chemistry Department, has been honored as Römer Lecturer (LMU München)
Prof. Dr. Markus Antonietti	Director of the Colloid Chemistry Department, has been honored as Staudinger-Durrer Lecturer (ETH Zürich)
Prof. Dr. Peter Fratzl	Director of the Department of Biomaterials, has been honored as Seidman Family Memorial Lecturer (Technion, Haifa, Israel)
Prof. Dr. Peter Fratzl	Director of the Department of Biomaterials, has been honored as Herbert Johnson Memorial Lecturer (Cornell University, Ithaka, USA)
Prof. Dr. Helmuth Möhwald	Director of the Interfaces Department, obtained the Prix-Gay-Lussac, which is awarded by the French Ministry for Research and Technology in collaboration with the Alexander Humboldt Foundation.
Prof. Dr. Helmuth Möhwald	Director of the Interfaces Department, obtained the Overbeek Medal of the European Colloid and Interface Society.

2007
Ruf an eine Universität
Appointments

Dr. Jan Kierfeld	Group Leader in the Department of Theory & Bio-Systems accepted a position as professor (W2) for Theoretical Physics at the Technical University Dortmund.

2008
Ehrungen/Mitgliedschaften/Honorarprofessuren
Honors/Memberships/Honorary Professorships

Prof. Dr. Markus Antonietti	Director of the Colloid Chemistry Department, received the ERC Advanced Grant, which is awarded with 2.5 million EUR, for a pioneering frontier research project in the area of sustainable chemistry.
Prof. Dr. Peter Fratzl	Director of the Department of Biomaterials, obtained together with the American chemical engineer Prof. Dr. Robert Langer, the Max Planck Research Award 2008 with prize money of, in total, 1.5 million Euros. They received the award for their research into structural-functional correlations in the development of biologically inspired materials and systems.
Prof. Dr. Peter Fratzl	Director of the Department of Biomaterials, has been honored as Erwin Ühlinger Memorial Lecturer (German Osteological Society)
Dr. Steffen Liepelt	Postdoc in the Department of Theory and Bio-Systems, received the Otto-Hahn Medal of the Max Planck Society.
Prof. Dr. Helmuth Möhwald	Director of the Department of Interfaces, obtained the degree of doctor honoris causa from the University Montpellier.
Dr. Melanie Müller	Member of the Department of Theory & Bio-Systems, obtained the Carl Ramsauer Award 2008 for dissertation on molecular motors.
Dr. Takashi Nakanishi	Group Leader in the Department of Interfaces, obtained the Award for Encouragement of Research in Polymer Science (The Society of Polymer Science, Yokohama, Japan).
Dr. Takashi Nakanishi	Group Leader in the Department of Interfaces, obtained the Outstanding Young Research Award on the Division of Colloids and Surface Chemistry (The Chemical Society of Japan, Fukuoka, Japan).
Prof. Dr. Peter Seeberger	Director of the Department of Biomolecular Systems, obtained the Karl Heinz Beckurts-Prize 2008 for the synthesis of antigens.
Prof. Dr. Peter Seeberger	Director of the Department of Biomolecular Systems, received the ERC Advanced Grant, which is awarded with 2.5 million EUR, for a pioneering frontier research project in the area of automated synthesis of heparin oligosaccharides.

2008

Ruf an eine Universität

Appointments

Dr. Himadri Shikar Gupta	Group Leader in the Department of Biomaterials, accepted a position as lecturer at the School of Engineering and Materials Science (Queen Mary University of London).
Dr. Rumen Krastev	Group Leader in the Department of Interfaces, accepted a position as .Group Leader for the development of new Biomaterials at the NMI Natural and Medical Sciences Institute at the University of Tübingen.
Dr. Dirk G. Kurth	Group Leader in the Department of Interfaces, accepted a position as professor (W2) for Chemical Technology of Material Synthesis at the University Würzburg.
Dr. Hubert Motschmann	Group Leader in the Department of Interfaces, accepted a position as professor (W2) for Physical Chemistry at the University Regensburg.
Dr. Arne Thomas	Group Leader in the Department of Colloid Chemistry, has been offered a professorship (W3) in Functional Materials at the Technical University Berlin.

2009

Ehrungen/Mitgliedschaften/Honorarprofessuren

Honors/Memberships/Honorary Professorships

Prof. Dr. Peter Seeberger	Director of the Department of Biomolecular Systems, obtained the Claude S. Hudson Award in Carbohydrate Chemistry (ACS)

Ruf an eine Universität

Appointments

Dr. Oskar Paris	Group Leader in the Department of Biomaterials, accepted a position as professor (W3) for physics at the Montanuniversität Leoben (Austria).

Wissenschaftliche Veröffentlichungen
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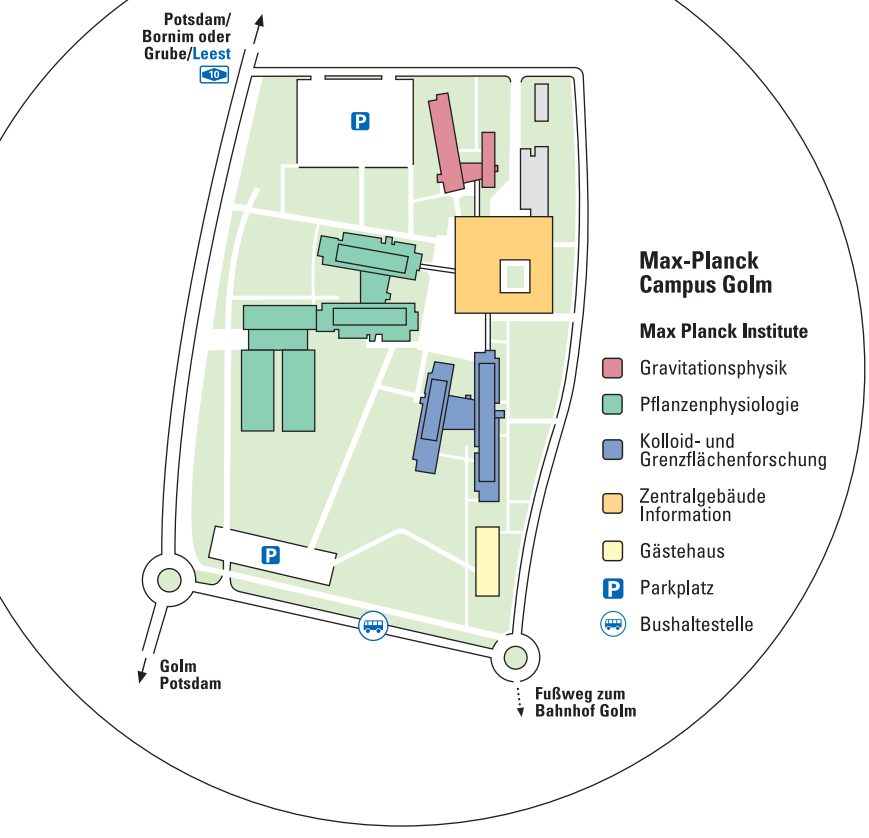

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