Max Planck Institute of Colloids and Interfaces

REPORT 2009-2010

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Max Planck Institute of Colloids and Interfaces

REPORT 2009-2010

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Vorwort

von links: Peter Fratzl, Markus Antonietti, Peter Seeberger, Helmuth Möhwald, Reinhard Lipowsky

Dieser Bericht beschreibt die Aktivitäten des Max-Planck-Instituts für Kolloid- und Grenzflächenforschung (MPIKG), das 1992 auf den Wurzeln zweier Akademieinstitute in den neuen Bundesländern gegründet wurde und seit 1999 im Wissenschaftspark Potsdam-Golm angesiedelt ist. Das MPIKG besteht zurzeit aus fünf Abteilungen, wobei die 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 MPIKG 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. sehr dünnen Strukturen im Nano- und Mikrometerbereich. Einerseits handelt es sich bei diesen Strukturen um eine ganze „Welt der versteckten Dimensionen“, andererseits bestimmt die komplexe Architektur und Dynamik dieser Strukturen das Verhalten von sehr viel größeren Systemen, wie z. B. Organismen.

Ein tieferes Verständnis von Kolloiden und Grenzflächen ist deshalb Schlüssel für zahlreiche Neuerungen, wie z. B. die 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 MPIKG erforscht werden, sind aus speziellen Molekülen aufgebaut, die nach dem Prinzip der Selbstorganisation „von selbst“ geordnete Strukturen aufbauen. Die Abteilungen „Biomolekulare Systeme“ (Peter Seeberger) und „Kolloidchemie“ (Markus Antonietti) beschäftigen sich schwerpunktmäßig mit der Chemie dieses Systemaufbaus.

In der Abteilung „Biomolekulare Systeme“, die im Jahr 2008 neu eingerichtet wurde, werden z. B. „maßgeschneiderte“ Zuckermoleküle synthetisiert und mit anderen molekularen Gruppen verknüpft. Diese komplexen Kohlehydrate können andere Kohlehydrate sowie Proteine und Antikörper an ihrem molekularen Aufbau erkennen und diskriminieren. Ein langfristiges Ziel ist dabei die Entwicklung von neuartigen Impfstoffen auf Zuckerbasis.

Die Abteilung „Kolloidchemie“ setzt wiederum 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 befestigt 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, von biologischen Wirkstoffen hin bis zum Korrosionsschutz.

Viele 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 z. B. die Methode der fokussierten Synchro-

tronstrahlung eingesetzt, die es erlaubt, die Struktur von Mikrodomänen des Materials 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 sind hier natürlich nur plakativ dargestellt und werden im Hauptteil dieses Berichts 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 MPIKG auch seine erfolgreiche Nachwuchsförderung weiter fortgesetzt. Inzwischen sind mehr als 50 ehemalige Mitarbeiter des MPIKG auf Professuren an Universitäten berufen worden.

Zum Schluss möchte ich nochmals erwähnen, dass wir 2010 mit der Planung des Erweiterungsgebäudes beginnen konnten und im Jahre 2013 mit seiner Fertigstellung rechnen. Diese Erweiterung beseitigt dann den wohl dringendsten Engpass des Institutes, Arbeitsplatz, da die Zahl unserer Mitarbeiter mit dem Erfolg und durch die erfolgreiche Einwerbung von Drittmitteln in den vergangenen Jahren stetig gewachsen ist.

An dieser Stelle möchte ich allen Kollegen und Mitarbeitern des MPIKG für ihre tatkräftige Unterstützung während der letzten beiden Jahre danken. Mein Dank gilt auch unserem wissenschaftlichen Beirat, der unsere Arbeit sehr kompetent und konstruktiv begleitet, und nicht zuletzt der Leitung der Max-Planck-Gesellschaft für die nachhaltige Unterstützung über die vielen Jahre hinweg.

Markus Antonietti
Geschäftsführender Direktor 2009-2010

Fotos S. 6-10: G. Gnaudschun

Preface

This report describes the recent activities of the Max Planck Institute of Colloids and Interfaces (MPICI), which was founded in 1992 as one of the first new Max Planck Institutes after the reunification of Germany. Since 1999 the MPICI is located in the Science Park Potsdam-Golm and currently consists of five departments. The department on „Biomolecular Systems" (Peter Seeberger) is temporarily accommodated at the FU Berlin until the extension of our building will be completed, presumably in 2013.

This preface provides a brief introduction to some basic aspects of the science 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 MPICI will be emphasized.

Colloids and interfaces consist of very small or thin structures with linear dimensions between nanometers and micrometers. On the one hand, the possible struxctures represent a „world of hidden dimensions". On the other hand, the dynamics and structures of these small entities determine the behavior of much larger systems such as organisms.

A more systematic understanding of colloids and interfaces is a prerequisite for many innovations, such as „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 MPICI are built up from special, even smaller molecules, which are using the principle of "self assembly" to construct ordered structures. The two departments on „Biomolecular Systems" (Peter Seeberger) and „Colloid Chemistry"(Markus Antonietti) put a focus of activity onto this "chemistry of system design".

The department „Biomolecular Systems", which has been newly established in 2008, synthesizes and designs sugar molecules and carbohydrates with well-defined and adjusted architectures. These complex macromolecules are able to specifically recognize and discriminate other macromolecules such as proteins and antibodies. A long-term goal of this research is to develop novel 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 self organization 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 nanoparticlecovering applicaitons 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 experimental 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 more detail in the main body of this report, which is organized according to the five departments of the MPICI. 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 MPICI also continued its successful higher academic education of young faculty. Indeed, more than 50 alumni of the MPICI have now taken up professorships in Germany and abroad.

Finally, I would like to mention that we have started the process of planning the new extension of our building in 2010, and the completion is to be expected in 2013. This extension will probably resolve our main problem, the shortage of working space at the institute, as the number of staff was continuously rising with the success, for instance measured in larger external funding.

I take this opportunity to thank all of my colleagues and associates at the MPICI 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 the Direction board of the Max Planck Society for their continuous support of our institute.

Markus Antonietti
Managing Director 2009-2010

Das Institut in Zahlen

Personal

Die Entwicklung der Zahlen ist wesentlich dadurch beeinflusst, dass ab 2009 die neue Abteilung „Biomolekulare Systeme“ voll funktionsfähig wurde und 2010 die Schrumpfung der Abteilung „Grenzflächen“ begann. **Abb. 1** zeigt daher einen leichten Anstieg des Stammpersonals nach 2008, aber schon 2008 einen sprunghaften Anstieg der Gesamtzahl der Mitarbeiter mit dem Aufbau der neuen Abteilung. Da dazu noch etwa 50 kurzzeitige Gäste kommen, bleibt die Raumsituation trotz der vorübergehenden Unterbringung der neuen Abteilung auf dem Campus der Freien Universität Berlin angespannt. Erst der Bezug des Erweiterungsbaus im Wissenschaftspark Potsdam-Golm, 2013/2014 wird eine Entlastung der Raumsituation bringen. Als Nebenbemerkung, 70% der Institutsangehörigen sind jünger als 35 Jahre, die übrigen verteilen sich etwa gleichmäßig über alle Altersklassen.

Abb. 2 zeigt ebenfalls einen drastischen Anstieg der Doktorandenzahlen in den letzten beiden Jahren, bei denen der Anteil deutscher Mitarbeiter (55%) leicht gegenüber Ausländern überwiegt. Da demgegenüber der Ausländeranteil bei den Postdoktoranden um 90% liegt (**Abb. 3**), beträgt dieser Anteil bei allen Wissenschaftlern um 70%. Von diesen stammen etwa 50% aus Europa, wobei in den letzten Jahren der Anteil der Westeuropäer gegenüber Osteuropäern leicht zugenommen hat (**Abb. 4**). Gegenüber früheren Jahren hat der Anteil an Amerikanern leicht zugenommen. Der Anteil an Chinesen sank dagegen etwas, vorwiegend, da zwei chinesische Gruppenleiter in ihr Heimatland bzw. Australien zurückgekehrt sind. Insgesamt hat sich die Verteilung der Nationalitäten damit dahingehend entwickelt, dass sich Ungleichgewichte reduzieren.

Budget

Auch die Entwicklung des Etats verzeichnete 2009 einen Sprung, da viele Investitionen und Baumaßnahmen mit Einrichtung der Abteilung „Biomolekulare Systeme“ fällig wurden (**Abb. 5**). Diese werden in Zukunft geringer sein und entsprechend erfolgte auch bereits 2010 eine geringere insti-

Fig. 1

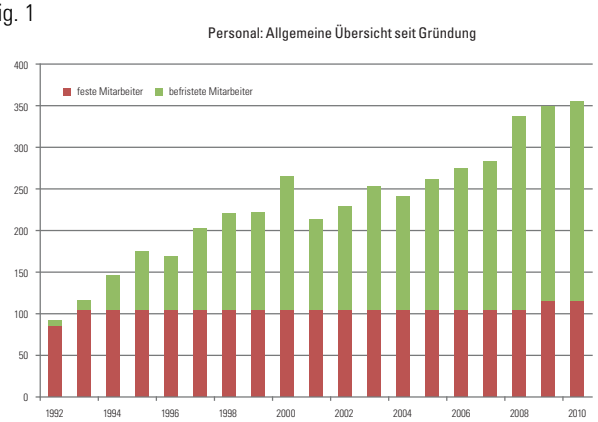


Fig. 3

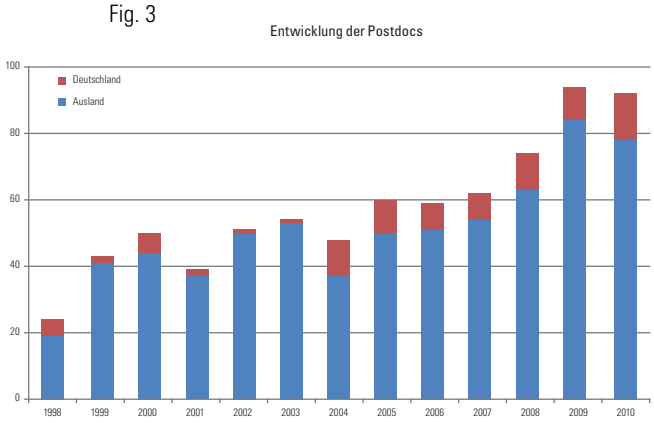


Fig. 2

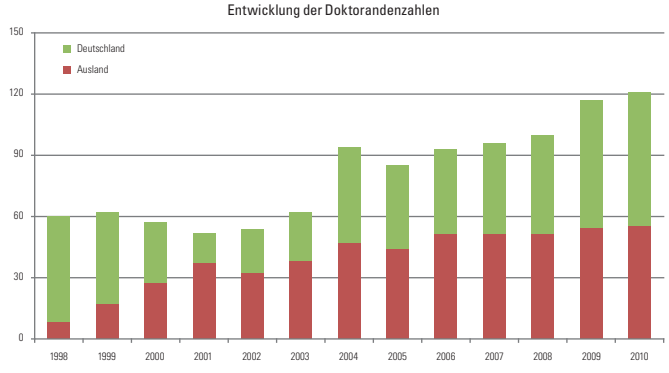
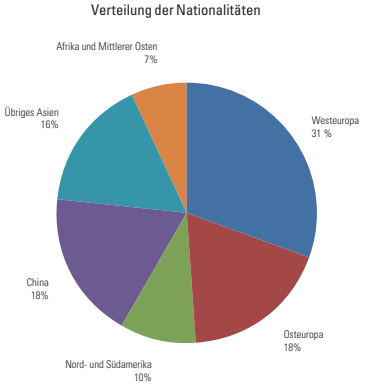


Fig. 4



tutionelle Förderung. Es fällt jedoch auf, dass mittlerweile der Drittmittelanteil am Etat etwa 25% erreicht hat mit stark steigender Tendenz. Bei diesen Drittmitteln hat sich der Anteil des BMBF und der DFG deutlich erhöht (**Abb. 6**). Dies ist insofern erstaunlich, da das Institut gerade bei diesen Institutionen von mehreren regulären Förderwegen ausgeschlossen ist. Dies konnte offenbar dadurch mehr als kompensiert werden, da die Wissenschaftler bei Anträgen in Sonderprogrammen besonders erfolgreich waren. Auch der EU-Anteil blieb erfreulich hoch und wird im nächsten Jahr 1 Mio. Euro übersteigen. Da das Institut keine Auftragsforschung durchführen will und darf, ist der Anteil direkter Industrieförderung mit weniger als 2% des Etats relativ gering, aber konstant. Dieses ist wünschenswert für ein Institut der Grundlagenforschung.

Wissenschaftliche Ergebnisse und deren Einfluss

Wir sind zwar ein Forschungsinstitut und keine Universität. Dennoch betrachten wir als wichtigsten Ertrag nicht Papier, sondern sehr gut ausgebildete junge Wissenschafter. Jährlich verlassen mehr als 5 Wissenschafter das Institut auf Professoren- oder äquivalente Stellen, 25-30 Doktoranden schließen ihre Arbeit ab und etwa 50 Postdoktoranden wechseln auf neue Stellen. Die Zahl der Publikationen hat mit etwa 300 einen „Sättigungswert" erreicht (**Abb. 7a**). Diese Zahl ist gut, aber nicht überragend für ein Institut mit dem Anspruch, an der Weltspitze zu stehen. Hervorragend jedoch ist die Zahl der Zitationen (**Abb. 7b**), mit denen sich das Institut mit jeder Institution vergleichbarer Größe weltweit vergleichen kann. Dies ist zudem bemerkenswert für eine junges Institut, da Zitationen auch auf Reputation beruhen und diese mit dem Alter wächst. Diese Zahlen sind letztlich auch dafür verantwortlich, dass Wissenschafter hochkompetitive Preise und Projekte gewannen und dass das Institut in Rankings wie denen der Alexander-von-Humboldt Stiftung einen Spitzenplatz einnimmt.

Fig. 5

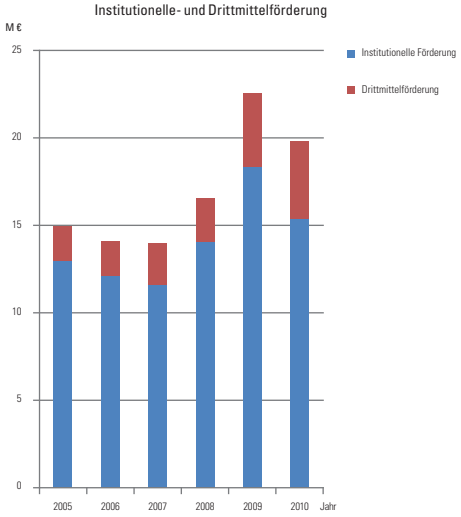


Fig. 6

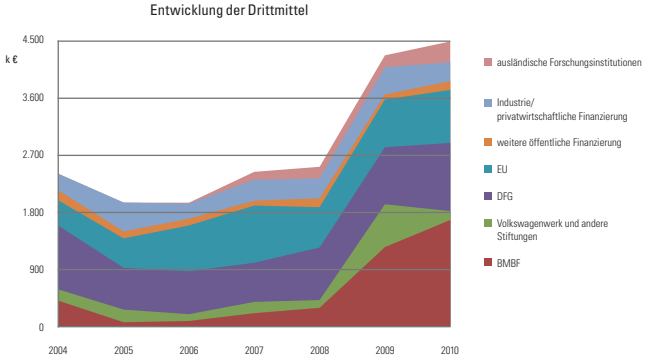


Fig. 7a

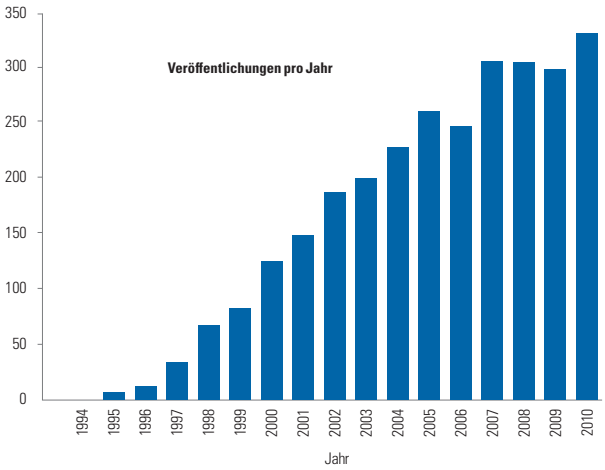
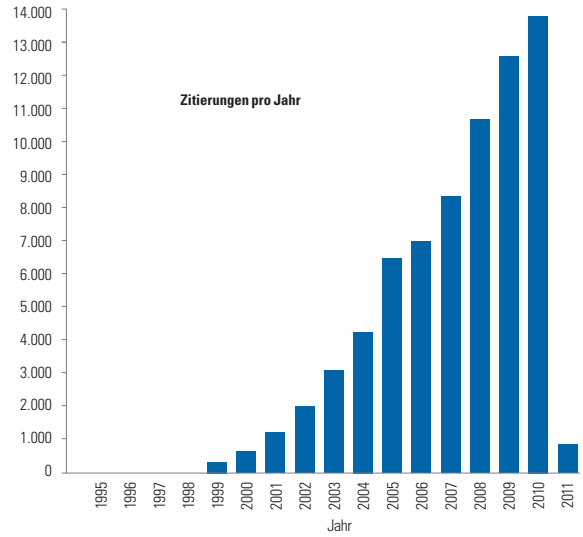


Fig. 7b



The Institute in Numbers

Personnel

The development of numbers is largely influenced by the fact that from 2009 the new department "Bimolecular Systems" came into full operation and that the downsizing of the department "Interfaces" began in 2010. Consequently **Fig. 1** shows a slight increase in staff after 2008 but already in 2008 a step-wise increase of employees paralleling the establishment of the 5th department. Since we host in addition about 50 short term guests there remains a tight pressure concerning space, although the new department could be established interim on the campus of the Free Univ. Berlin. This situation will only be relieved after the institute can move into the extension building in 2013/2014. As a side note 70% of the institute members are aged below 35, the others rather-evenly distributed over all ages. For reasons as above **Fig. 2** shows a drastic increase of the number of graduate students in the last 2 years with the fraction of Germans (55%) slightly above that of foreigners. This differs for the postdocs where the fraction of foreigners is around 90% (**Fig. 3**), and therefore their fraction concerning all scientists is around 70%. Among them about 50% come from Europe, and in recent years the fraction of Western Europeans has slightly increased compared to Eastern Europeans (**Fig. 4**). With respect to previous years the fraction of Americans has slightly increased. That of Chinese, on the other hand, has decreased predominantly since two Chinese group leaders have returned to there home country, respectively Australia. Altogether the distribution of nationalities has developed in a way that imbalances have been levelled off.

Budget

Also the budget development exhibits a step in 2009 where many investments and construction measures were needed to establish the department "Biomolecular Systems". These investments will be reduced in future and consequently the institutional funding decayed again in 2010 (**Fig. 5**). On the other hand it is remarkable that third party funding has meanwhile exceeded a fraction of 25%. Among them the fraction

Fig. 1

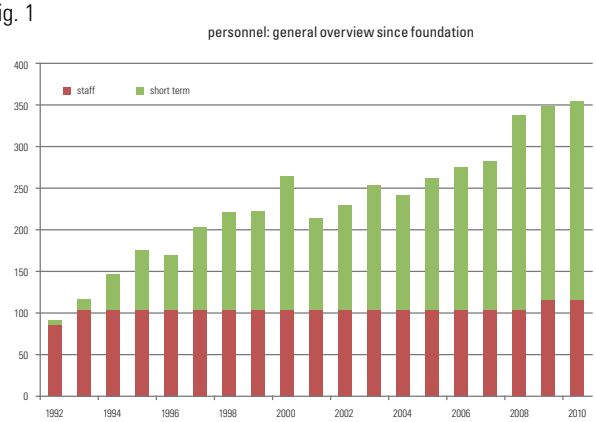


Fig. 2

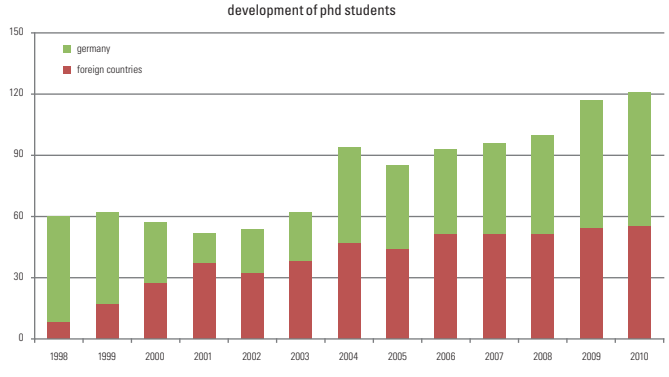


Fig. 3

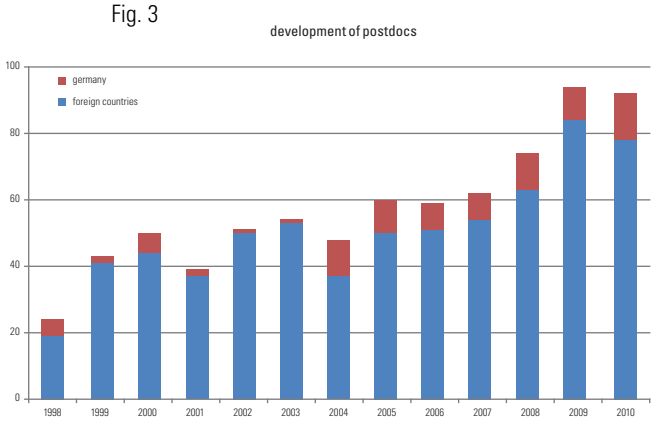
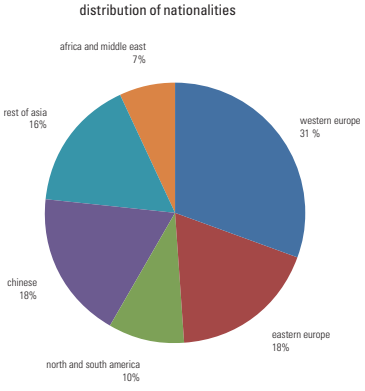


Fig. 4



of the federal ministry of education and technology (BMBF) and of the German Science Foundation (DFG) have experienced a most drastic increase (**Fig. 6**). This is surprising since the institute is explicitly excluded from many regular funding schemes of these institutions. Apparently this could be more than compensated, since scientists have been especially successful with applications in special programmes. It is also gratifying that the funding from European Union remained high and this year will exceed 1 Mio. Euros. Because the institute does not want and is not allowed to perform contractual research for industry their contribution is below 2% of the budget, which is rather low and stable. This is desirable for an institute with a basic science mission.

Scientific Results and Impact

Although being a research institute and no university we consider the most important result not paper but well-trained young scientists. Annually more than 5 scientists leave the institute on professor positions or equivalent ones, 25-30 PhD students finish their theses and about 50 Postdocs leave on new positions. The number of publications has arrived at a "saturation value" around 300 (**Fig. 7a**). This is a good but not an overwhelming number for an institute that claims to be world-top. Overwhelming, however is the number of citations (**Fig. 7b**) with which the institute need not fear a comparison with any unit of comparable size world-wide. This is in addition remarkable for a rather young institute since citations are also based on reputation and this increases with age. These numbers are basically the reason that scientists win highly competitive awards and projects and that the institute is top-seeded in rankings like those of the Alexander-von-Humboldt foundation.

Fig. 5

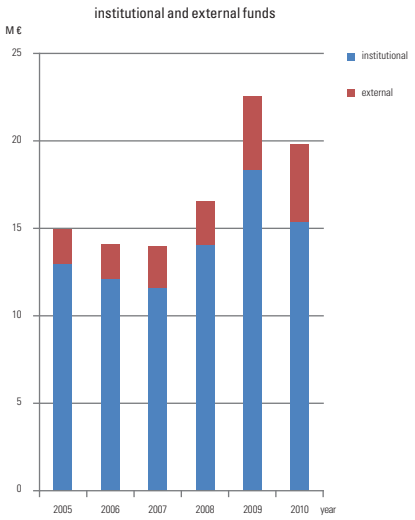


Fig. 6

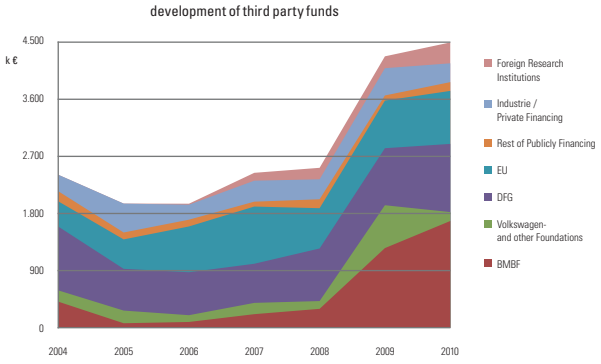


Fig. 7a

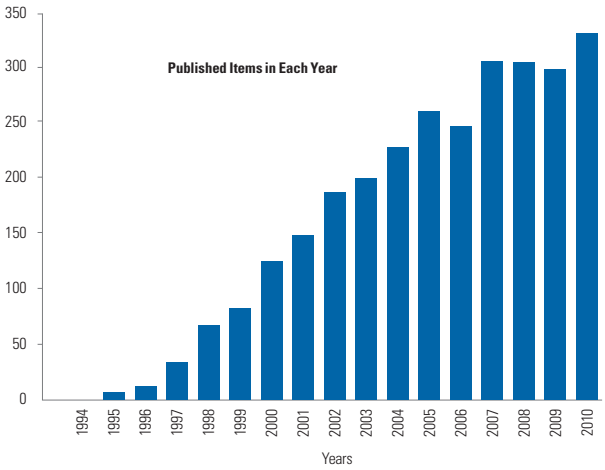
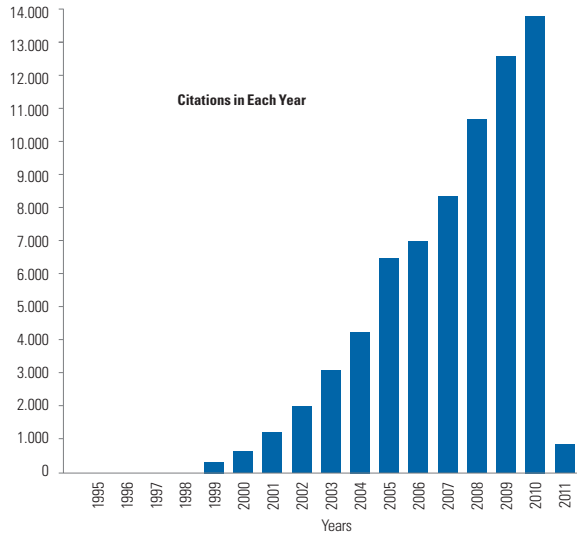


Fig. 7b



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

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

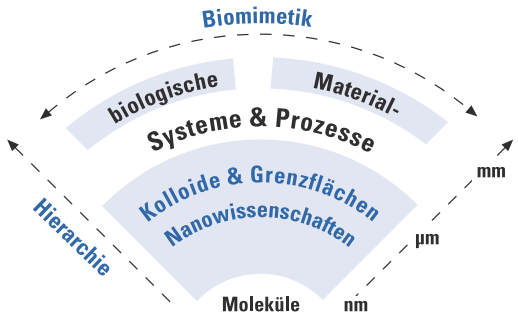


Abb. 1: Die Forschung am MPIKG beschäftigt sich mit Strukturen und Prozessen, die zwischen dem Nano- und Mikrometerbereich liegen, d.h. mit dem traditionellen Bereich der Kolloid- und Grenzflächenforschung, der viele Ebenen, angefangen von Molekülen bis hin zu biomimetischen Materialien und biologischen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

Die vielfältige Funktionsweise biologischer Systeme hängt größtenteils von Struktur und Dynamik der Kolloide und Grenzflächen auf submikroskopischer Ebene ab. Eine begrenzte Zahl von Aminosäuren, Nukleotiden und Monosacchariden bilden eine Vielzahl biologischer Polymere mit nanometergroßen Strukturen. Diese verbinden sich zu Filamenten, Membranen, Ribosomen und verschiedenen Biokolloiden, 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.

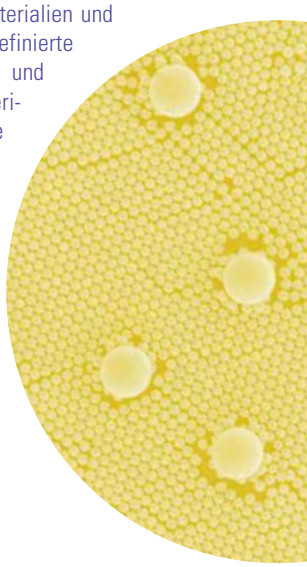
Kolloide und Grenzflächen

Die aktuelle Forschung am Institut konzentriert sich auf komplexe, natürliche und künstliche Mehrkomponenten-Systeme und wendet dabei Techniken aus der Physik, Chemie, den Materialwissenschaften und Biowissenschaften an. Wir untersuchen die Struktur- bzw. Funktionsbeziehungen in hierarchischen biologischen Materialien; wir konstruieren experimentelle Modellsysteme; Schließlich entwickeln und konstruieren wir theoretische Modelle.

Das Wechselspiel von Experiment und Theorie hilft, ein tieferes Verständnis der Ordnung von Kolloid- und Grenzflächensystemen zu erlangen. Diese Erkenntnisse werden für die Verbesserung des Systemdesigns, die Leistungsoptimierung und die Erhöhung der Zuverlässigkeit eingesetzt. Somit hat die Grundlagenforschung des MPI KG direkten Einfluss auf die Entwicklung bahnbrechender Technologien und deren zukunftsweisende Anwendungen. Ein besseres Verständnis biologischer Systeme ist ein erster wichtiger Schritt und hat Einfluss auf die biomedizinischen Wissenschaften. So wurden beispielsweise kolloidbasierte Wirkstoff-Transportsysteme entwickelt oder krankheitsbedingte Veränderungen des Knochenmaterials charakterisiert. Zudem werden synthetische Kohlenhydrate entwickelt, die zur Herstellung von Impfstoffen und Diagnostika eingesetzt werden.

Das Institut hat Weltklasseniveau in der Analyse, Synthese und der theoretischen Modellbildung harter und weicher Materialien erreicht. Die Kompetenz im Bereich der Synthese ist besonders breit: kristalline, oxidische Nanopartikel und neue Kohlenstoffvarianten werden mit Hilfe hydrothermaler und hochtemperierter Karbonisierung hergestellt. Diese Partikel bilden die Basis für neuartige Sensoren und funktionale Beschichtungen oder können direkt in der Chromatographie, der Katalyse bzw. als Füllmaterial in hybriden Materialien angewendet werden. Neue Polymerisationsmethoden zur Herstellung polymerer Nanopartikel sowie die Heterophasen-Polymerisation mit deutlich geringerem Einfluss auf die Umwelt werden für nanoskopische Einkapselungen, Hybridisierungen oder grenzflächengesteuerte Synthesen benutzt.

Für die Grundlagenforschung, aber auch für technische Anwendungen ist neben den weichen und harten Strukturen das kontrollierte Einbringen von nanoskopisch kleinsten Poren als Transportkanäle in Füllmaterialien und Filmen bedeutsam. Die klar definierte Entwicklung geeigneter Strukturen und Porengrößen in kristallinen Materialien ermöglicht es uns, verbesserte Elektroden, Sensorbeschichtungen, photovoltaische und elektrochrome Geräte herzustellen.



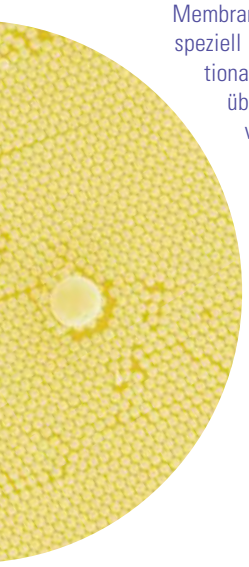
Viele Eigenschaften und Interaktionen der kolloidalen Systeme werden durch ihre hoch spezifische Oberfläche beeinflusst. Deshalb sind Prozesse, die sich auf der Oberfläche abspielen, von besonderem Interesse. Darin eingeschlossen sind der dynamische Austausch von Materie zwischen Grenzfläche und Masse, die Struktur von Wasser und Hydrathüllen in der Nähe von Oberflächen, Enzymkatalyse genauso wie Oberflächenkristallisation. Synthetisch beeinflusste Partikeloberflächen verändern ihre Aktivität und Funktionalität, können aber somit als Bausteine für supramolekulare Strukturen dienen, die dann weiter in der supramolekularen Chemie als funktionale Filme, reaktive Kapseln oder selbstreparierende Beschichtungen Anwendung finden.

Hierarchische Strukturen

Zwei sehr verschiedene Wege, um kolloidale Strukturen erzeugen und die Lücke zwischen Molekülen und Materialien oder Bauteilen zu schließen, werden am MPIKG verfolgt: Die Bottom-Up Methode beinhaltet Polymerisation, Selbstorganisation sowie Partikelbildung und -wachstum, die Top-down Methode hingegen Dispersion, Druck, Lithographie und Modellbildung. Die Methoden der Poylmersynthese helfen, komplexe Materialien zu erzeugen, die entweder komplett organisch sind, wie etwa Blockcopolymere, oder organisch-anorganische Hybride.

Amphiphile Blockcopolymere weisen synthetische Analogien zu Lipidmolekülen auf, die in der Natur für die Bildung von Membranen, Vesikeln und komplexeren räumlichen Anordnungen verantwortlich sind. 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 MPIKG wurde eine überaus effektive Methode für die Bildung von eher komplexen Grenzflächenstrukturen entwickelt, die auf der nacheinander folgenden Ablagerung von negativ und positiv geladenen Polyelektrolyten basiert.

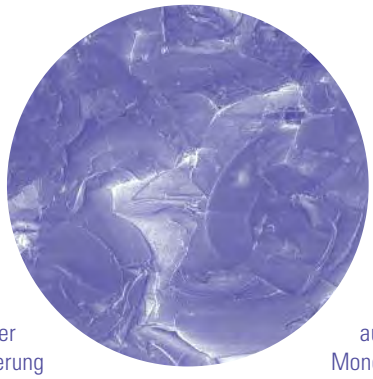
Darüber hinaus wird am Institut ein großes Spektrum an experimentellen Methoden genutzt, um Struktur und Dynamik von Kolloiden und Grenzflächen zu charakterisieren. Zudem werden verschiedene Methoden der chemischen Analyse verwendet. Eine entscheidende Herausforderung bildet die simultane Bestimmung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

Biomimetische Systeme

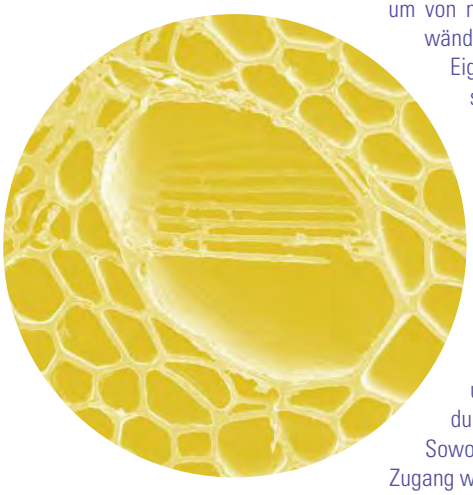
Biomimetische Forschung erstreckt sich von den lebenden Systemen zu den Materialien und umgekehrt (siehe **Abb. 1**). Die Analyse der Struktur- Funktionsbeziehungen in den Zellen und der extrazellulären Matrix, vom physikalisch-chemischen Standpunkt, ergibt notwendige Informationen für den Aufbau von biomimetischen Systemen. Künstliche biomimetische Systeme werden genutzt, um etwa 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 Gerüsten. Auf der kolloidalen Ebene treffen verschiedene Komponenten aufeinander, die durch geschlossene Membranen und unterschiedliche Gerüste gebildet und durch vernetzte Fasern aufgebaut werden. Hauptfunktion der Membrankomponenten ist es, den Raum in einzelne Bereiche zu teilen und den selektiven Transport

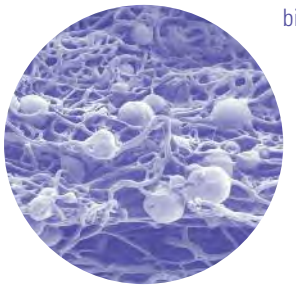


zwischen den Komponenten zu ermöglichen. Die primäre Aufgabe der Faserngerüste ist die Umstrukturierung der Komponenten und die Neuorganisation der räumlichen Anordnung.



Die Forschung am MPIKG beinhaltet auch das Studium von natürlichen Materialien wie Pflanzenzellwände, Bindegewebe, Knochen sowie deren Eigenschaften und Fähigkeit zu heilen und sich an wechselnde Umgebungsbedingungen anzupassen. Die Arbeit an biomimetischen Systemen schließt den Aufbau und das Studium verschiedener Komponenten mit ein: Tröpfchen in Mikro- und Miniemulsionen, Vesikeln aus Lipiden oder polymeren Doppelschichten aus Polyelektrolyt-Multilagen bestehenden Kapseln. In diesen Verbindungen 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 herzustellen, 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 zu biomimetischen 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.

Mit der Gründung der Abteilung „Biomolekulare Systeme“ im Jahr 2009 hat das Institut einen weiteren Schwerpunkt im Bereich der Forschung an der Grenze von Chemie und Biologie gesetzt. Wiederum steht die Synthese von komplexen Molekülen, Kohlenhydraten und Glykokonjugaten im Fokus. Synthetisch erzeugte Zucker dienen dazu, Prozesse an Zelloberflächen zu studieren, die diese Biopolymere enthalten. Die Impfstoffentwicklung, diagnostische Verfahren und grundlegende Immunologie werden durch die automatische Synthese von Zuckern ermöglicht. Das Anbringen von synthetischen Zuckern an Polymeren, verschiedenen Oberflächen und Nanopartikeln ermöglicht es, neue Materialien herzustellen, die Anwendung in der Polymerchemie und der Biomedizin finden.

Das Institut konnte in den letzten Jahren grundlegende Fragen angehen, die sich jetzt als lebensnahe Anwendungen in so verschiedenen Gebieten wie der Energie, Materialforschung und Biomedizin wiederfinden. Die methodologisch einwandfreie Basis ist das Fundament für starke, fachübergreifende Interaktionen am MPIKG, die Einsichten in Gebiete erlauben wie sonst nirgendwo. Viele interessante Durchbrüche erwarten uns in den kommenden Jahren.

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

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

Colloid and interface science focuses on the size range between "nano" and "micro" –„the world of hidden dimensions" – and bridges the gap between molecules and biomimetic materials or biological tissues. Two scientific aspects are key in this realm (**Fig. 1**). Structural and dynamical hierarchies need to be understood to connect the nanoregime with much larger scales. Secondly, basic mechanisms and general principles have to be elucidated to provide an unified conceptual framework for both biomimetic and biological systems.

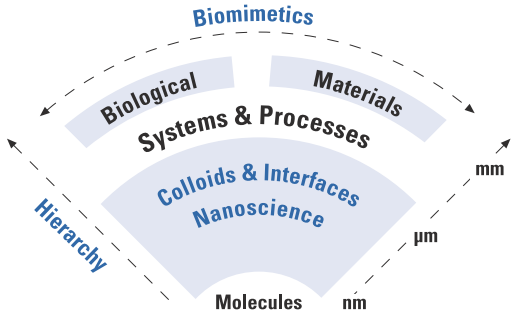


Fig. 1: Research at the MPI-CI focuses on structures and processes in the size range between nano and micro, the traditional domain of colloid and interface science. Therefore, questions involving molecules to biomimetic materials and biological tissues.

The functional versatility of biological systems depends primarily on the structure and dynamics of colloids and interfaces in the nanoregime. Relatively few amino acids, nucleotides and monosaccharides form a multitude of biological polymers with sizes in the nanometer range. These biopolymers further assemble into filaments, membranes, and various biocolloids that may contain mineral elements. Cells in turn are incorporate these higher order assemblies and are the basis of any living organism. The step from biopolymers (few nanometers) to living cells (many micrometers) is crucial for constructing the complex architecture of organisms. Analogously, the function of biomimetic materials and their mechanical, optical or magnetic properties depend largely on the structures built in the nano- to micrometer size range.

Colloids and Interfaces

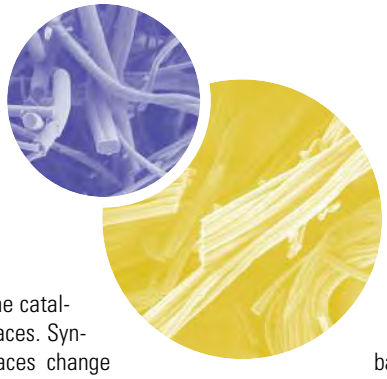
Current research at the MPI-CI focuses on complex, natural and artificial multicomponent systems, employing techniques from physics, chemistry, materials science and the biosciences. We study structure/function relationships in hierarchical biological materials; We construct experimental model systems and characerize them; Finally, we construct and analyze theoretical models.

This interplay between experiment and theory helps to gain a better understanding of colloidal and interfacial systems. These insights help to improve system design, to optimize performance, and to increase reliability. Consequently, basic research at the MPI-CI has direct impact on the development of cutting edge technologies for the applications of tomorrow. A better understanding of biological systems is an important first step towards impacting on the biomedical sciences. In this sense, colloidal drug-delivery systems have been developed, understanding the changes in bone material arising from disease help medical treatment and synthetic carbohydrates are being developed as vaccines and diagnostis.

The institute has gained world-class expertise in the analysis, synthesis and theoretical modeling of hard and soft matter. The synthetic expertise is particularly broad: Crystalline, oxidic nanoparticles and new types of carbon are prepared via hydrothermal and high temperature carbonization pathways. The particles are the basis for novel sensors and functional coatings or can be directly applied in chromatography, catalysis, or fillers in hybrid materials. New polymerization methods for polymer nanoparticles and heterophase polymerization with greatly reduced environmental impact are utilized for nanoscale encapsulation, hybridization and interface driven synthesis.

In addition to soft and hard structures, the controlled generation of nanoscopic pore channel systems into bulk materials and films holds many promises for fundamental science and applications Rational, templated design of architecture and pore size in crystalline materials enables us to make better electrodes, sensing layers, photovoltaic and electrochromic devices.

Many interactions and properties of colloidal systems are determined by their high specific surface. Therefore, processes that occur at the surface are of particular interest including dynamics of exchange of matter between interface and bulk,, the structure of water and hydration shells



near surfaces, recognition and enzyme catalysis as well as crystallization at surfaces. Synthetically manipulated particle surfaces change their interfacial activity, biofunctionalization and can serve as building blocks for supramolecular assemblies as well as micro- and nanocontainers. Supramolecular chemistry aids in the preparation of functional films, responsive capsules and self-repairing coatings.

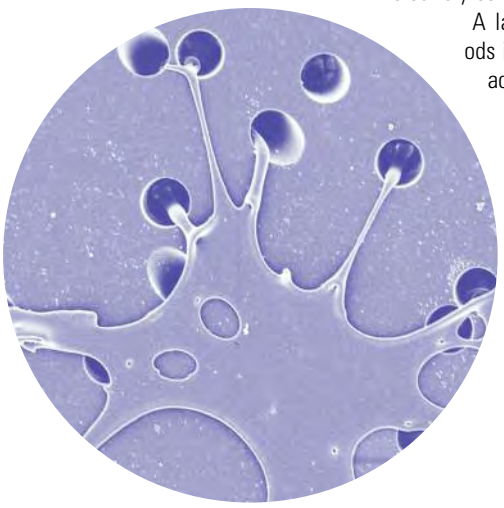
Hierarchical Structures

Two fundamentally different routes to construct colloidal structures and bridge the gap between molecules and materials or tissues are currently pursued at the MPI-CI. Bottom-up approaches rely on polymerization, self-assembly, particle nucleation and growth. Top-down approaches include dispersing, printing, lithography, and prototyping. Polymer synthesis methods help to create complex materials that are either fully organic, such as block copolymers or organic-inorganic hybrids.

Amphiphilic block co-polymers provide synthetic analogues of lipid molecules that form bilayer membranes, vesicles and more complex spatial compartments in Nature. 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 top-down approach is based on the thermodynamics of interfaces and membranes, the bottom-up method starts from coarse-grained models for the molecular building blocks and their interactions.

A long-term goal is the creation of multifunctional biomaterials that are based on the fact that biomimetic systems such as synthetic polymers can interact with biological system itself – they can bind to cells. Synthetic scaffolds can help to spatially arrange cells into tissues. Integrating different levels of control into new multifunctional biomaterials that are organized in a hierarchical manner would help us to address the different structural levels of the biological systems.

Active Biomimetic Systems are another emerging topic: Biological systems are versatile since they can actively adjust their spatial structure on the nano- and microscale. Active nanostructures such as filament monomers and molecular motors that can catalyze exergonic chemical reactions are the basis fort hese events. It is now possible to imitate these processes in biomimetic model systems and to study them in a systematic manner.

The International Max-Planck Research School on Biomimetic Systems supports the research on biomimetic systems by improving the training of young researchers in this emerging field. A Marie-Curie Early Stage Training Network, complements the educational activities in this area.

With the arrival of the new department "Biomolecular Systems" in 2009 the Institute added strength at the chemistry-biology interface. Again, the synthesis of complex molecules, carbohydrates and glycoconjugates in this case, is at the center of the activities. Synthetic sugars serve to study processes on the surface of cells that involve these biopolmyers. Vaccine development, diagnostic approaches and fundamental immunology all are enabled by the automated synthesis of sugars. The placement of synthetic sugars on polymers and many different surfaces and nanoparticles provides opportunities for new materials that can be applied to problems associated with biomedical sciences and polmer chemistry.

The institute has been able to address fundamental questions in the past few years that are now beginning to translate into real-life applications in areas as diverse as energy, materials and biomedical research. The sound methodological foundation provides the basis for strong cross-disciplinary interactions that provide insights in areas that cannot be tackled elsewhere. Many interesting breakthroughs await us in the coming years.

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

Wissenschaftliche Beziehungen

Kooperationen mit Universitäten:
Zwischen dem Max-Planck-Institut für Kolloid- und Grenzflächenforschung (MPIKG) 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). Im April 2009 wurde Matias Bargheer zum W3-Professor an der Universität Potsdam (UP) ernannt. Die Kooperation mit dem MPIKG bleibt bestehen.

Das Institut war von 1998 bis 2009 über den Sonderforschungsbereich (SFB) 448 „Mesoskopische Verbundsysteme“ mit der Universität Potsdam und allen drei Berliner Universitäten verknüpft. Es ist beteiligt am Elitenetzwerk „Unifying Concepts in Catalysis“, das von der TU Berlin geleitet wird. Über den SFB 760 „Musculoskeletal Regeneration“, der von der Charité - Universitätsmedizin Berlin koordiniert wird sowie den SFB 765 „Multivalenz als chemisches Organisations- und Wirkprinzip“, von der FU koordiniert, kooperiert es ferner mit der FU Berlin und dem Helmholtz-Zentrum Geesthacht (Institut für Polymerforschung). 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). Zudem koordiniert Prof. Fratzl das DFG-Schwerpunktprogramm SPP 1420 „Biomimetische Materialforschung“, an dem mehr als zehn Universitäten sowie Max-Planck-Institute beteiligt sind, das Bauprinzipien und Herstellung von neuartigen, hierarchisch strukturierten Materialien untersucht, die auf natürlichen Vorbildern basieren.

Eine Plattform für die Untersuchung biologischer Proben mit Synchrotronstrahlung wird in enger Kooperation mit der Universität Heidelberg 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 Networks of Excellence-(NoE), Marie Curie- und Specific Target Research Projects (STREP)-Maßnahmen. Insgesamt laufen zurzeit fünf EU-Projekte innerhalb des 6. und sieben EU-Projekte innerhalb des 7. Rahmenprogramms, davon zwei ERC Advanced Grants.

Bilaterale- und Kooperationsprojekte bestehen zur Zeit unter der Förderung der European Space Agency (ESA), der NATO, 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), des Schweizer Nationalfonds, der Schweizerischen Eidgenossenschaft sowie der VW-Stiftung mit Frankreich, der Gemeinschaft Unabhängiger Staaten (GUS), Griechenland, Großbritannien, Irland, Italien, Israel, Niederlande, Norwegen, Portugal, Polen, Schweiz, Schweden, Spanien, 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 liefen in 2004 die aus dem strategischen Innovationsfonds der MPG geförderten Projekte „Plant Cell Wall“ und „ENERCHEM (Nanochemische Konzepte einer nachhaltigen Energieversorgung)“ sehr erfolgreich an. ENERCHEM ist ein Forschungsverbund von fünf Max-Planck-Instituten zur Entwicklung nanochemischer Lösungen für eine nachhaltige Energieversorgung. Das gemeinsam von den Max-Planck-Instituten für Kolloid- und Grenzflächenforschung, Festkörperforschung, Polymerforschung, Kohlenforschung und dem Fritz-Haber-Institut gegründete Projekt wurde in der ersten Phase bis 2009 von Prof. Antonietti geleitet. Die Forschungsinitiative wird von der MPG mit insgesamt rund 4 Mio. Euro aus dem Strategischen Innovationsfonds gefördert.

Darüber hinaus kooperierte das Institut mit den Fraunhofer-Instituten für Angewandte Polymerforschung und Biomedizinische Technologie und der Universität Potsdam bis 2010 in dem Projekt "Bioaktive Grenzflächen". Der MPG-Anteil (Strategiefonds) am Gesamtvolumen von 3.5 Mio. Euro betrug 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, Merck, Servier, der Beiersdorf AG und AstraZeneca UK. Das Institut hält gegenwärtig 43 Patente. Im Zeitraum von 1993-2000 erfolgten insgesamt sieben Ausgründungen: Capsulution Nanoscience AG, Colloid GmbH, Nanocraft GmbH, Optrel, Riegler & Kirstein, Sinterface und Oxidion GmbH.

Perspektiven

In den letzten Jahren hat sich die Forschung an biomimetischen Systemen zunehmend als eine gemeinsame Klammer zwischen den Abteilungen entwickelt. Unterstützt wird die Verbreiterung des Themas durch die IMPRS „Biomimetic Systems" sowie durch die Mitwirkung in entsprechenden EU-Netzen. Mit Einrichtung der Abteilung „Biomolekulare Systeme" hat das Institut sein Spektrum erweitert und den Fokus auf Biowissenschaften verstärkt.

Editorial Boards und Fachbeiräte

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.

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- Biophysical Journal (R. Lipowsky)
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- Austrian Nano Initiative (H. Möhwald, Beirat und Jury)
- Bayreuther Zentrum für Kolloid- und Grenzflächenforschung (H. Möhwald)
- Berlin-Brandenburg School of Regenerative Therapies BSRT (P. Fratzl, Lenkungsausschuss)
- Biofibres Materials Centre, Stockholm (H. Möhwald)
- DECHEMA Arbeitsgruppe über „Chemische Nanotechnologie" (H. Möhwald)
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- Fondation ICFRC, International Center for Frontier Research in Chemistry, Strasbourg (H. Möhwald)
- Fraunhofer-Institut für Angewandte Polymerforschung (H. Möhwald)
- FWF Fonds zur Förderung der Wissenschaftlichen Forschung (P. Fratzl, Aufsichtsrat)
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- Institute of Science and Technology Austria (P. Fratzl, Fachbeirat)
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- PETRA III microfocus beamline (P Fratzl)
- Photon Science Committee DESY (P. Fratzl, Chair bis 2009)
- Radeboud University Nijmwegen (P. Seeberger)
- Tesfa-Ilg Foundation (P. Seeberger, Gründungsmitglied)
- University College London, Dept. of Chemistry (P. Seeberger)
- WYSS Institute for Bioinspired Engeneering at Harvard University (P. Fratzl, Fachbeirat)

Scientific Relations

National Cooperations:
Co-operations with Universities

The Max Planck Institute of Colloids and Interfaces (MPIKG) 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). In April 2009 Matias Bargheer was appointed as W3 professor at the University Potsdam (UP). The cooperation with the institute will go on.

Besides this the institute was connected with the University Potsdam and with all three Berlin universities through the German Research Foundation (DFG) priority program "Mesoscopic Composites" from 1998 to 2009. It is also involved in the Cluster of Excellence "Unifying Concepts in Catalysis", which is co-ordinated by the Technical University Berlin. Furthermore the MPICI cooperates in the new SFB program "Musculoskeletal Regenaration" (co-ordinated by Charité, Medical University, Berlin) and the by the FU coordinated SFB 765 "Multivalent Display" with the Free University Berlin and the Institute of Polymer Research at the Helmholtz-Zentrum Geesthacht. It is also a 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. On top of this Prof. Fratzl co-ordinates the DFG priority program SPP 1420 "Biomimetic Materials Research", in which more than ten universities as well as Max Planck Institutes take part. The aim is to explore the possibility of generating new material classes of great potential by combining the degrees of freedom of hierarchical structuring inspired by nature with the variety of materials offered by engineering.

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 seven within the 7th framework program, including two ERC Advanced Grants.

Beyond the collaborations described there exist bilateral and co-operation projects under assistance of the European Space Agency (ESA), the NATO, 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), Swiss National Science Foundation (SNSF) and the VW - Stiftung with Commonwealth of Independent States (CIS), France, Greece, Ireland, Italy, Israel, the Netherlands, Norway, Poland, Portugal, Switzerland, Sweden, Ukraine, United Kingdom (UK) and the 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 projects "Plant Cell Wall" and "EnerChem", funded by the strategic innovation funds of the Max Planck Society have been successfully started in 2004. EnerChem is a research association of five Max Planck Institutes which was coordinated by Prof. Antonietti in the first phase till 2009. The research initiative is funded with 4. Mill. EUR.

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" lasted till 2010. The research project was funded with altogether 3.5 Mill EUR. The part of the strategic innovation funds of the Max Planck Society amounted to 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, Merck, Servier, der Beiersdorf AG und AstraZeneca UK. At present the MPIKG upholds 43 patents. In the period from 1993-2006 seven spin-offs have been launched: Capsulution Nanoscience AG, Colloid GmbH, Nanocraft GmbH, Optrel, Riegler & Kirstein, Sinterface and Oxidion GmbH.

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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- Berlin-Brandenburg School of Regenerative Therapies, BSRT (P. Fratzl, steering commitee)
- Biofibres Materials Centre, Stockholm (H. Möhwald)
- DECHEMA Research Group on "Chemical Nanotechnology" (H. Möhwald)
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- German Colloid Society (H. Möhwald, President)
- The Helmholtz Centre Berlin for Materials and Energy (Peter Fratzl, Board of Directors)
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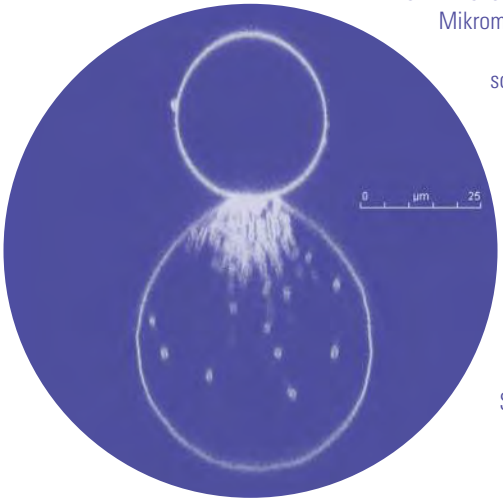
Internationale Max Planck Research School (IMPRS) über Biommetische Systeme

Das Max-Planck-Institut für Kolloid- und Grenzflächenforschung (MPIKG) 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 bestand.

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 MPIKG erforscht biomimetische Systeme im Bereich supramolekularer und kolloidaler Größenordnungen. Diese Systeme werden hauptsächlich durch die innere Architektur von Zellen inspiriert, enthalten viele Makromoleküle und weiche Nanostrukturen mit linearen Dimensionen zwischen einigen Nano- und vielen Mikrometern.



Die aktuelle Forschung über biomimetische Systeme am MPIKG beinhaltet folgende Themenbereiche: Wasserstruktur; Polyelektrolyte und andere wasserlösliche Polymere; flexible Membranen mit mehreren Lipidkomponenten; Diblock-Copolymerschichten und Polyelektrolyt-Multischichten; Membranfusion, aktiver Transport von molekularen Motoren; Regulation von zellulären Prozessen; Biomineralisation und Knochen; Netzwerkdynamik und Evolution; Systembiologische Projekte.

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 Abteilung für „Biomaterialien" des MPIKG nahm 2003 ihre Arbeit auf und beteiligt sich seitdem ebenfalls an der Schule. Die Struktur der IMPRS bestand in dieser Weise bis zur Mitte des Jahres 2006.

Mit dem zweiten Bewilligungszeitraum (ab Mitte 2006) kamen weitere Gruppen hinzu: zwei Gruppen der Universität Potsdam, drei Gruppen der Humboldt-Universität zu Berlin, zwei Gruppen des Fraunhofer-Instituts für Biomedizinische Technik (IBMT) und eine Gruppe des Fraunhofer-Instituts für Angewandte Polymerforschung (IAP).

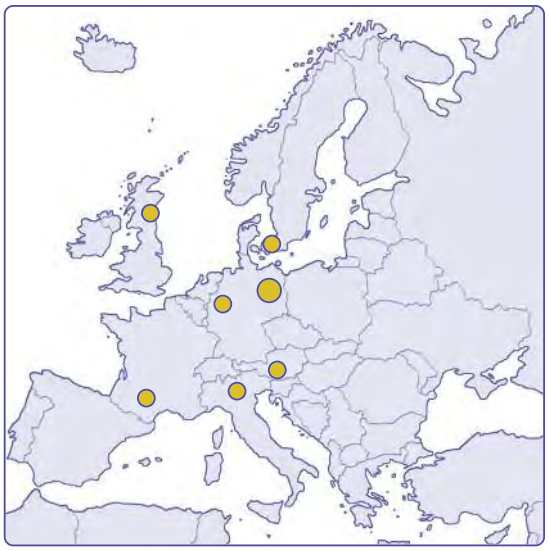
Das Fraunhofer-Institut für Biomedizinische Technik ist im Sommer 2006 in den Wissenschaftspark Potsdam-Golm gezogen. Die Gruppen der Humboldt- Universität zu Berlin befinden sich in Berlin-Adlershof.

Anfang 2009 wurde die neue Abteilung für „Biomolekulare Systeme" des MPIKG eingerichtet, die zur Zeit noch provisorisch an der Freien Universität Berlin untergebracht ist.

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. 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.

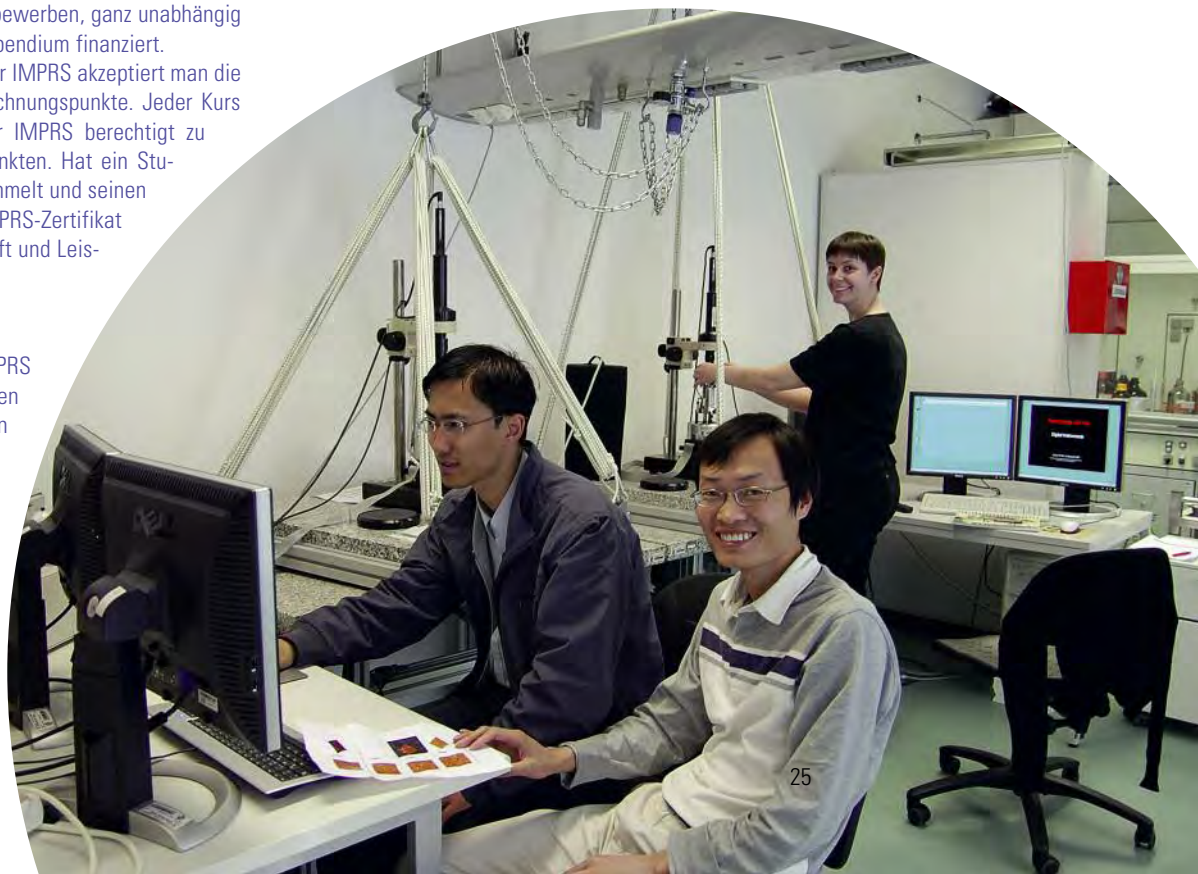
Doktorgrad
Studenten, die Mitglieder der IMPRS sind, sind immer als Doktoranden an einer der Partneruniversitäten eingeschrieben. Sie verteidigen ihre Arbeit vor einer Kommission, die aus Fakultätsmitgliedern der Universität und des MPI für Kolloid- und Grenzflächenforschung besteht und den Regeln der 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; regulation of cellular processes; biomineralization and bone; networks dynamics and evolution; systems biology projects.

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.

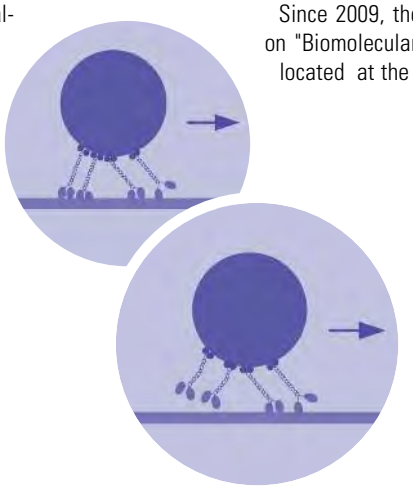
Thus, already in 1999, one of us (R.L.) submitted a proposal for the International Max Planck Research School on Biomimetic Systems (IMPRS) to the President of the Max Planck Society. This proposal was approved and the school started with its first semester in the year 2000. The school was originally 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.

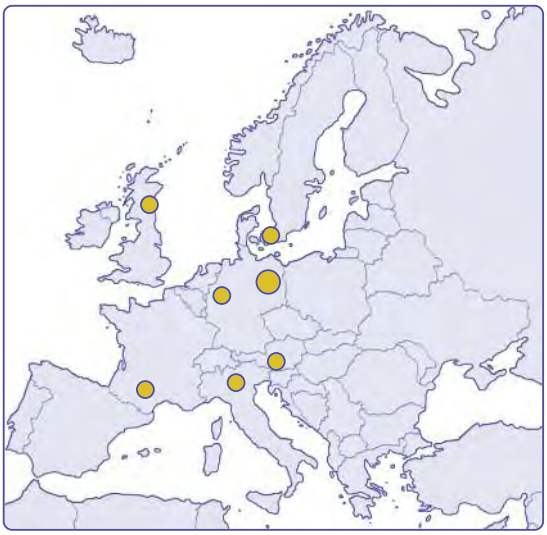
Partners of the School

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.

Since 2009, the MPICI has the new department on "Biomolecular Systems", which is temporarily located at the Free University 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. 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 related to 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 all over 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, dem Golm Innovationszentrum GO:IN sowie dem Brandenburgischen Landeshauptarchiv 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 2011 am 10. September stattfinden.

Seit dem Jahr 2000 richtet das Bundesministerium für Bildung und Forschung (BMBF) Wissenschaftsjahre aus. Ziel solcher Themenjahre ist es, das Interesse der Öffentlichkeit an Wissenschaft zu fördern und zu verstärken. Das Wissenschaftsjahr 2010 widmete sich der Zukunft der Energie. Höhepunkt des Themenjahres war der Tag der Energie am 25. September 2010. Die Max-Planck-Institute für Molekulare Pflanzenphysiologie und Kolloid- und Grenzflächenforschung sowie zahlreiche Partner luden dazu in den Wissenschaftspark Potsdam-Golm ein. Interessierte Besucher konnten mit Hilfe von „Grüner Kohle“ aus Biomasse, Energiepflanzen, geregelten LED-Straßenleuchten oder Wasserstoff aus Mikroalgen in die Zukunft der Energie eintauchen.

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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Fotos: „Tag der offenen Türen“ und „Tag der Energie“, K. Schulze, (MPIKG)

Press and Public Relations

Press and Public Relations at the Max Planck Institute of Colloids and Interfaces serve as the interface between the scientists' work and the public. We inform you about the research results, and want to create an independent, positive image and thus trust in scientific work. Simultaneously we try to bridge the gap between research institution and general public and hence get new impetus and ideas. We promote the perception of our research among the community, the press, government, corporate partners, prospective students, alumni and our own internal community. It is a matter of great importance that not only the scientific community but in fact anyone interested in modern science should have the opportunity to get an idea about the aims of our institute. Attention, interest and finally trust in science must be one of our most important concerns.

Therefore we inform journalists with profound news and background knowledge about current research. To pursue this task press releases are edited, 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 Research Campus 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 Golm Innovation Center GO:IN and the Brandenburg Main State Archive on September 10. There will be lab tours, popular talks and scientific demonstrations providing an excellent opportunity for everybody to experience scientific activity at first hand.

A further important event was the Science Year 2010. Under the slogan "The Future of Energy" the Federal Ministry of Education and Research (BMBF), in co-operation with German science and industry, was showcasing scientists' creativity in tackling the challenge of building a safe, cost-effective and climate-friendly energy sector. On Saturday, 25 September 2010, research institutions, universities, companies, museums and many other organizations around the country opened their doors for the nation-wide Day of Energy. In the process, they offered a look at the fascinating world of energy research, energy use and energy applications.

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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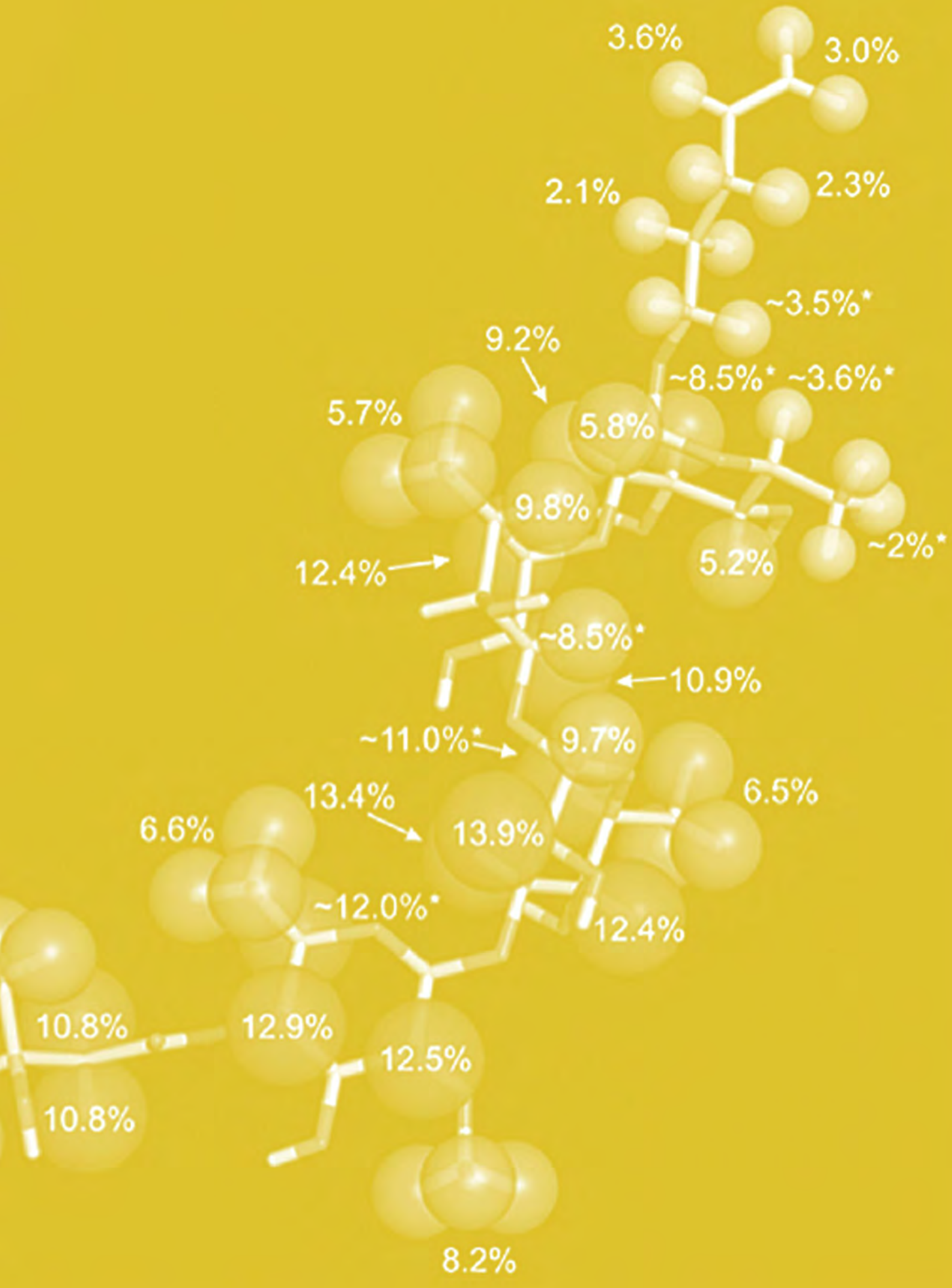
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→ Glycoimmunology
→ Carbohydrate Synthesis
→ Glycoproteomics
→ Precision Polymers and Polymeric Biomimetics
→ Biomolecular Systems
→ (GPIs) and Glycoproteins

BIOMOLECULAR SYSTEMS

Research in the Department of Biomolecular Systems

Peter H. Seeberger 14.11.1966
1989: Vordiplom (Univ. Erlangen-Nürnberg)
1995: PhD, Biochemistry (University of Colorado, Boulder)
1995-1997: Research Fellow (Memorial Sloan-Kettering Cancer Center)
1998-2003: Assistant and Associate Professor (Massachusetts Institute of Technology, MIT, Cambridge, USA)
2003-2009: Professor (Swiss Federal Institute of Technology (ETH) Zurich, Switzerland)
Since 2003: Affiliate Professor (The Burnham Institute for Medical Research, La Jolla, USA)
Since 2009: Director, Department of Biomolecular Systems (Max Planck Institute of Colloids and Interfaces)

The Department for Biomolecular Systems, founded in 2009, conducts research at the **interface of chemistry, engineering, biology, immunology and medicine.** The approach is transdisciplinary and interactive between the groups in the department that cover different areas of expertise. 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. In the past two years groups have been established to cover the other core technology, glycan sequencing and glycomics (Dr. Kolarich) in order to identify glycans of biological importance and to assess the role of glycans *in vivo* (Dr. Lepenies, glycoimmunology). 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.

Materials aspects related to carbohydrates have become increasingly important since our move. The group of Dr. Hartmann merges polymer synthesis with our biomolecule expertise and in close collaboration with the glycoimmunologists, the *in vivo* activity of the complex synthetic molecules is assessed. Continuous-flow synthesis has been drastically increasing in importance and is beginning to pervade all aspects of synthetic chemistry. Important collaborations for the synthesis of colloidal polymers have yielded exciting results and many other applications of the flow paradigm from organic to nanoparticle synthesis and polymer chemistry are currently progressing rapidly.

Automated Synthesis of Carbohydrates

The past two years, since our arrival in Potsdam the Department of Biomolecular Systems we have greatly expended on the first automated oligosaccharide synthesizer (Science 2001, 291, 1523). Now, the entire process is streamlined and based on a set of building blocks, a polymeric support and new linker as well as a new instrument, access to complex oligosaccahrides is not only fast but requires little technical expertise. The Department is beginning to close 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.

The concept has been extended now to the automated synthesis of glycosaminoglycans, a class of biologically extremely important oligosacchrides (e.g. heparin). With the help of an ERC Advanced grant a new linker that is cleaved via continuous flow photochemistry, a new synthesis instrument and novel synthetic schemes were combined to create a process that speeds synthesis times from many months down to three days! This breakthrough will open completely new areas for biology but also material sciences involving growth factor interactions.

Synthetic Tools for Glycobiology
Using the synthetic oligosaccharides, we have expanded on the preparation of tools such as glycan microarrays, glycan nanoparticles, glacan dendrimers and glycans on polymers and fibers as well as inorganic materials such as quantum dots and zeolithes. These tools are now commonly used by the glycobiologists in the department to elucidate fundamental processes such as the entry mechanism of parasites into host cells.

Synthetic Carbohydrate Vaccines
Using synthetic oligosaccharides as basis, the department is now advancing a large number of carbohydrate-conjugate vaccine projects. While in the past the focus was almost exclusively on the synthesis, we are now conducting also conjugation and formulation as well as immunological assessment. With this integrative approach, vaccine development has accelerated in house and a number of molecules are rapidly advancing. Following earlier work on malaria (Nature 2002, 418, 785) a host of antigens against bacterial diseases are now at different stages of development.

Carbohydrate-based Nanotechnology
The attachment of carbohydrates to the surface to nanoparticles and surfaces has seen rapid progress in the department since the move to Potsdam. With the ability to characterize the products of our studies much more thoroughly and faster than previously, metalloglycodendrimers, glyco-quantum dots, glyco-gold islands and glyco-fullerenols have been prepared and are now beginning to see applications in biology and even in applications towards clinical use.

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.

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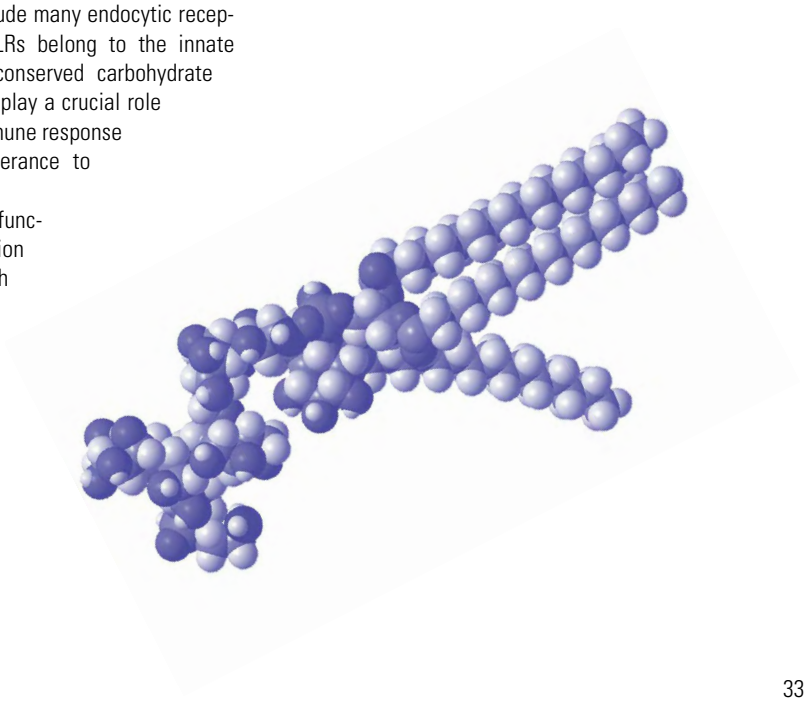

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Targeting C-type Lectins to Modulate Immune Responses

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Host defense relies on a concerted action of both innate immunity and adaptive immunity. In this interplay, innate immunity encompasses numerous rapid defense mechanisms to infections and other challenges. Cells of the innate immune system use a variety of so-called pattern recognition receptors to recognize molecular structures shared between pathogens. C-type lectin receptors (CLRs) are carbohydrate-binding receptors that recognize glycan structures on pathogens (as shown in **Fig. 1**).

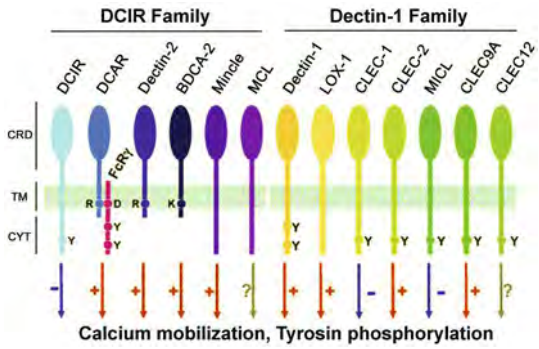

Fig. 1: C-type lectin receptors (CLRs) in the immune system are expressed by antigen-presenting cells, particularly dendritic cells. They are crucial for antigen uptake and cell activation. Dendritic cell immunoreceptor (DCIR) and DC-associated C-type lectin (Dectin-1) are the prototypes for CLRs on dendritic cells.

They are predominantly expressed on antigen-presenting cells such as dendritic cells and bind carbohydrate structures in a Ca^{2+}-dependent manner. Many endocytic receptors, collectins, and selectins belong to the CLR superfamily. In the immune system, CLRs are mainly involved in pathogen recognition. Additionally, they are important for the maintenance of tolerance to autoantigens **[1]**. The main goals of our group are, first, to understand in detail how CLRs influence inflammatory processes *in vivo* and, second, to exploit CLRs for cell-specific targeting and immunomodulation.

Targeting of C-type Lectin Receptors

Targeting glycan-binding receptors is an attractive approach to inhibit competitive binding of natural ligands or to deliver drugs specifically into cells expressing these receptors. However, since glycan-binding proteins exhibit only a low affinity for their ligands, multivalent interactions are often required to exhibit biological effects **[2]**. In proof-of-principle experiments, we showed that a specific targeting of the CLR asialoglycoprotein receptor (ASGP-R) can be achieved by using multivalent carbohydrate ligands **[3]**. ASGP-R is a glycoprotein that binds to desialylated (i.e. galactosyl-terminal) glycoproteins and is expressed exclusively in hepatic parenchymal cells. When hepatocytes were incubated with quantum dots (QDs) capped with D-galactose (D-Gal) or control sugars, preferential uptake of D-Gal QDs was observed *in vitro* caused by ASGP-R-mediated endocytosis. Similar results were obtained when galactose dendrimers and liposomes that displayed D-GalNAc-terminated lipids were employed to target ASGPR **[4]**. Thus, dendrimers and glycoliposomes displaying multiple D-Gal/D-GalNAc residues are suitable hepatocyte-specific targeting systems. Moreover, intravenous injection of QDs capped with terminal D-Gal or D-GalN residues into mice resulted in specific sequestration of those QDs in the liver (see **Fig. 2**).

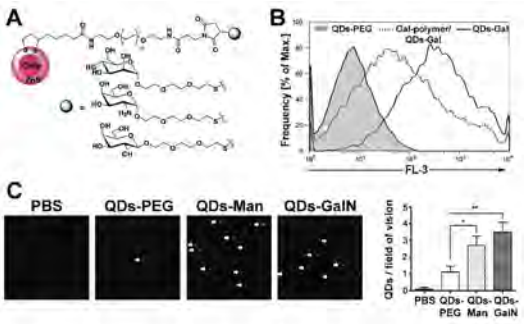

Fig. 2: Targeting of asialoglycoprotein receptor (ASGP-R) using carbohydrate-capped quantum dots. A, Quantum dots (QDs) and sugars used in this study (n = 45–50). B, Specific uptake of D-Gal capped QDs by HepG2 cells. For inhibition of Gal-QDs binding and uptake, HepG2 cells were preincubated with a PLL-Gal-polymer. C, Specific liver sequestration of D-mannose (D-Man) and D-galactosamine (D-GalN) capped QDs. Mice were i.v. injected with PBS, 2.5 nmol PEG-QDs or QDs capped with D-Man or D-GalN. 2 h after injection mice were sacrificed, paraffin sections of the livers were prepared, and QD sequestration was visualized by fluorescence microscopy [3].

In conclusion, carbohydrate-protein interactions exhibit specificity and, thus, glycan-binding receptors such as CLRs may be valuable targets for cell-specific drug and gene delivery *in vivo*.

Immunomodulation via C-type Lectin Receptors

Carbohydrate synthesis represents a useful tool to develop vaccines against infectious diseases or cancer and to synthesize ligands for glycan-binding proteins **[5]**. Additionally, synthetic carbohydrates may be used as "danger signals" for the immune system to provoke a pro-inflammatory immune response. This is of particular interest for the design of novel adjuvants. We aimed at targeting CLRs expressed by dendrit-

ic cells by using synthetic carbohydrates chemically coupled to model antigens. For this purpose, phosphatidylinositol mannoside (PIM) glycans, biologically important glycoconjugates present in the cell wall of *Mycobacterium tuberculosis*, were used. The synthetic PIM glycans were immobilized on microarray slides and were shown to bind to the dendritic cell specific intercellular adhesion molecule-grabbing non-integrin receptor (DC-SIGN). Interestingly, the PIM glycans served as efficient immune stimulators and increased the efficacy of vaccines. Immunization of mice with model antigens covalently coupled to the PIM glycans led to increased antibody levels and T cell effector functions such as cytokine release compared to well-established adjuvants (as shown in **Fig. 3**).

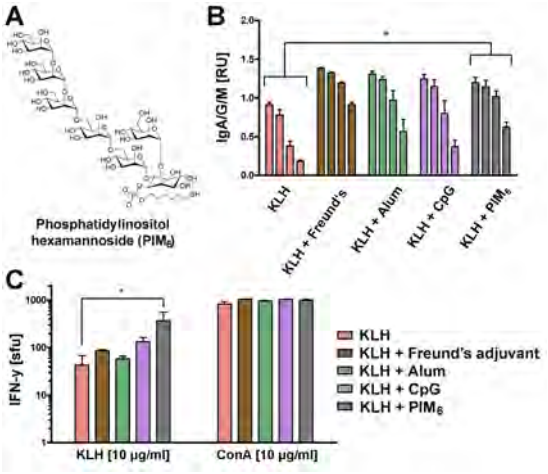

Fig. 3: CLR targeting with synthetic PIM glycan. A, Structure of the synthetic PIM6 glycan from Mycobacterium tuberculosis. B, C57BL/6 mice were s.c. immunized with keyhole limpet hemocyanin (KLH) in the presence of the indicated adjuvants or after covalent linkage to PIM6. On day 17 after immunization, levels of anti-KLH antibodies were measured by ELISA in serial dilutions of the sera. C, On day 20, splenocytes were stimulated with KLH or concanavalin A (ConA) and the frequency of IFN-producing cells was determined by ELISpot [6].

This finding indicates that synthetic glycan structures indeed have a great potential as adjuvant candidates **[6]**.

Functionalization of surfaces with glycans is another way to influence cellular functions such as proliferation or differentiation and to modulate inflammatory responses. In this respect, we could show that D-mannose-functionalized PCL/PPfpMA fiber meshes enhanced the cytokine production by murine macrophages upon lipopolysaccharide (LPS) stimulation whereas control fibers functionalized with galactose- or aminoethanol had no effect on cytokine production **[7]**.

Tools for Analyzing the Function of C-type Lectins

To investigate the role of C-type lectin receptors in inflammatory processes *in vivo*, we are currently establishing mouse models for infection and autoimmunity. To identify yet unknown carbohydrate ligands for CLRs, additional tools are needed. One such tool that we have already constructed is CLR-Ig fusion proteins consisting of the extracellular domain of the respective CLR and the constant fragment of antibody molecules (shown in **Fig. 4**).

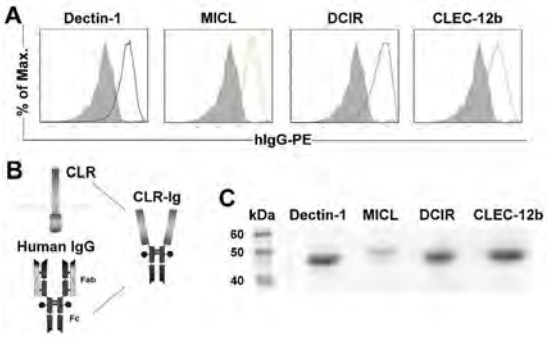

Fig. 4: A, Eukaryotic expression of different CLR-immunoglobulin (CLR-Ig) fusion proteins in CHO cells. B, Schematic representation of CLR-Ig construction. C, Western Blot to detect CLR-Ig protein levels in CHO cells. CLR-Ig fusion proteins were expressed for the following CLRs: CLEC-1, CLEC-2, DCIR, DCAR, MCL, Mincle, Dectin-2, Dectin-1, Lox-1, CLEC-9a, MICL, CLEC-12b, MGL.

These fusion proteins are then used to screen libraries of glycan structures by glycan array, a method that allows for testing carbohydrate-protein interactions in a high-throughput manner. Using the glycan array platform, we will identify new CLR ligands that are further characterized for their immunomodulatory properties in cell-based assays and *in vivo*. We are also producing monoclonal anti-CLR antibodies with either blocking or agonistic activity to be administered as CLR agonists or antagonists in mouse models of infection and autoimmunity.

Finally, the physiological function of a protein of interest can be best investigated in animals lacking the respective protein. Consequently, CLR-deficient mice are currently being generated in our group. In those mice, the functional copy of a CLR gene is swapped for the mutated (inactive) version in mouse embryonic stem cells. These "knockout mice" will provide a deeper insight in how CLRs act *in vivo* and which role CLRs play in infectious and autoimmune diseases.

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Automated Solid Phase Synthesis of Complex Carbohydrates

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Oligosaccharides are one of the most important classes of biomolecules. They are involved in a variety of biochemical processes, such as cell differentiation, proliferation and adhesion, inflammation and immune responses. **[1, 2]** In higher organisms, proteins are posttranslationally modified by the attachment of different oligosaccharides, influencing the physical and chemical properties of a glycoprotein such as folding, solubility, charge, and half-life. Due to their microheterogeneity the isolation of pure glycoproteins from natural sources is a tedious process and many functions of these complex carbohydrates are poorly understood. Another promising approach is the use of specific carbohydrates on the surface of parasites, bacteria or cancer cells for the creation of vaccines. However, it is often difficult or even impossible to cultivate those organisms as source for the desired carbohydrate structures. Chemical synthesis is a powerful tool in order to furnish sufficient amounts of pure oligosaccharides for biological evaluation or vaccine production. However, the classical solution phase synthesis of oligosaccharides is often a time-consuming task and usually requires a special strategy for each molecule.

Automated Solid Phase Synthesis

To overcome these problems solid phase synthesis is a powerful alternative approach. A solid support functionalized with a linker carries the growing oligosaccharide chain during the synthesis. During this process a building block is glycosylated to the linker followed by removal of a temporary protecting group for the next chain elongation step (see **Fig. 1**). By using a large excess of reagents complete conversion in glycosylation and deprotection reactions can be achieved. The number of chromatographic purification steps is reduced to a minimum because excess reagents can be removed simply by washing. After complete assembly of the oligosaccharide chain, the product is cleaved from solid support followed by global deprotection of permanent protecting groups. This approach could lead to carbohydrate structures of interest, that could be further used for the synthesis of glycoconjugates or glycoarrays (see **Fig. 1**).

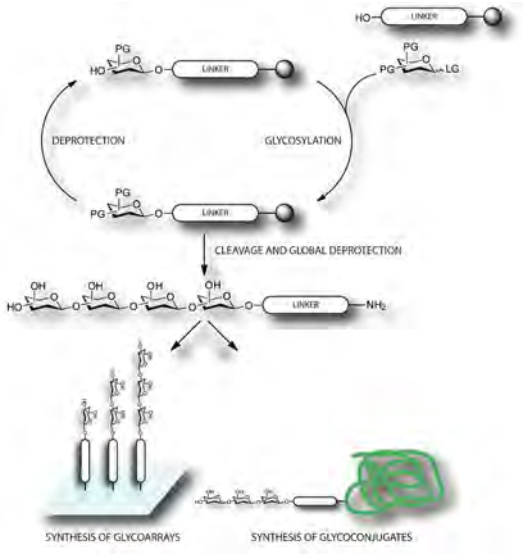

Fig. 1: Schematic Overview of Solid-Supported Oligosaccharide Synthesis: Connected via a linker the oligosaccharide chain is elongated on the solid support in alternating glycosylation and deprotection reactions. After cleavage from the resin and global deprotection the oligosaccharides can be used for the synthesis of glycoconjugates or glycoarrays.

Fully Automated Carbohydrate Synthesizer

The repetitive character of solid-supported oligosaccharide synthesis makes this process suitable for automation like in peptide or oligonucleotide synthesis. The first syntheses were performed successfully in a modified ABI peptide synthesizer, which features were adapted for carbohydrate chemistry. **[3]** With the help of this setup it was shown that automated synthesis reduces the expenditure of time dramatically **[4]** and an anti-malaria toxin was already obtained. An anti-malaria vaccine was obtained from this GPI anchor derivative and it is expected to enter clinical trials in 2011. **[5]** To meet the specific requirements of carbohydrate synthesis properly, a fully automated carbohydrate synthesizer was developed (see **Fig. 2**). **[6]**

Fig. 2: Automated Oligosaccharide Synthesizer: The reactions take place in the reaction vessel (5) and are completely controlled by a PC (1) software and a controller (9). The temperature can be adjusted by a cryostat (2) and the reagents (3) are delivered via syringe pumps (6). Solvents (8) to wash the resin are delivered and removed by Ar pressure (7) and solenoid valves (4) and reaction solutions can be collected in a fraction collector (10) for further analysis.

Reactions take place in a double-jacketed reaction vessel which allows for cooling and heating of the reaction partners. The solvents used for washing the resin between the individual reaction steps are delivered and removed by argon pressure via solenoid valves and reagents and building blocks are added with the help of syringe pumps, rotary valves and loops. The reaction solutions can be discarded or collected in the fraction collector for later analyses, such as Fmoc quantification for evaluating the coupling efficiency. The entire process is fully controlled using special programs, which are composed of various modules for the different chemical reactions and washing steps. A controller acts as an interface between the computer and all components of the synthesizer. This setup allows the complete synthesis of oligosaccharides without further intervention.

Automatically Obtained Oligosaccharides

In combination with the development of the new prototype of synthesizer, also a versatile linker was designed. **[6]** The linker enables the use of a greater variety of building blocks and was used for the automated solid phase synthesis of β-1,6-linked glucosamine oligosaccharides (see **Fig. 3**).

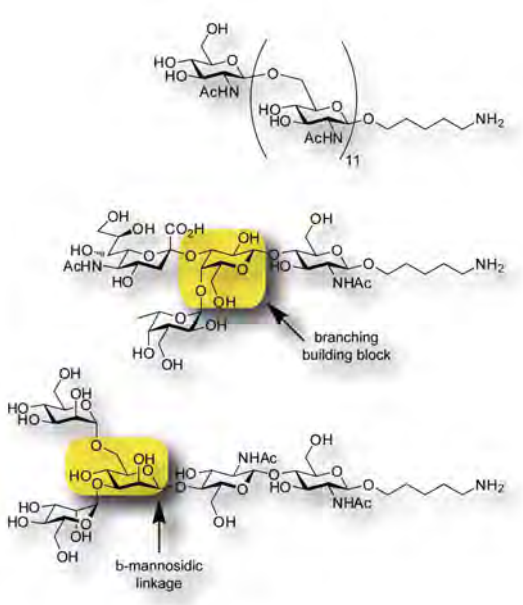

Fig. 3: Automatically Synthesized Oligosaccharides: The β-1,6-glucosamine was synthesized in different chain lengths with a miximum of 12 sugar residues. By using orthogonal protecting groups, a branched Sialyl Lewis X tetrasaccharide was obtained. For the synthesis of the core pentasaccharide of N-glycans the challenging β-mannosidic linkage was successfully glycosylated on solid support.

These carbohydrate structures are for instance involved in biofilm formation of *Staphylococcus* bacteria. Oligomers with up to twelve sugar residues were synthesized in 43% yield after cleavage from solid support. By using orthogonally removable protecting groups, a branched Sialyl Lewis X tetrasaccharide was obtained. Another automated synthesis furnished the common core pentasaccharide structure of *N*-linked protein glycosylations. This *N*-glycan contains a challenging β-mannosidic linkage, which was introduced in former approaches by the use of a disaccharide building block, already bearing this concerning linkage. Using an appropriate glycosylating agent **[7]** the *N*-glycan core pentasaccharide was synthesized for the first time on solid support from monosaccharide building blocks. All these syntheses proove, that the automated oligosaccharide synthesizer can be used to obtain complex and biologically relevant carbohydrate structures.

Automated Synthesis of Glycosaminoglycans

A current project is the automated synthesis of glycosaminoglycans that are linear oligosaccharides containing a disaccharide repeating unit. Glycosaminoglycans bear sulfate and carboxylic acid groups and thus are highly negatively charged molecules. Due to this fact, their synthesis belongs to one of the greatest challenges for carbohydrate chemists. In order to avoid many solution synthesis steps after the assembly of the oligosaccharide chain, sulfation and partial deprotection steps should be carried out on solid support. This leads to a high demand on linker and building blocks for the automated synthesis of glycosaminoglycans. As a proof of principle, the synthesis of different chondroitin sulfates (see **Fig. 4**)

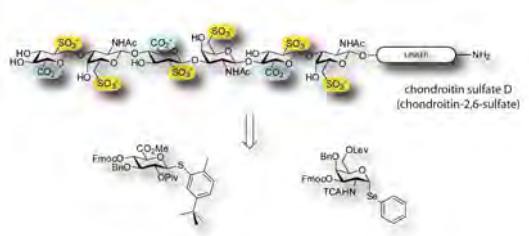

Fig. 4: Retrosynthetical Analysis of Chondroitn Sulfate D: After the assembly of the linear oligosaccharide chain the sulfate groups should be introduced on the solid support. Carboxylic esters should be hydrolyzed in an automated way followed by introduction of native N-acetates. This approach should be transferred to the synthesis of different glycosaminoglycans.

was chosen. In future reaction conditions could be transferred to the automated synthesis of different glycosaminoglycans by using a set of appropriate building blocks.

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Quantitative Glycomics and Glycoproteomics for Biomarker Discovery

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Lead Actors of Life: Glycoproteins

If the cell was a movie, DNA is the director, with proteins taking the lead roles. However, production of a blockbuster requires the perfectly organised actions of the whole film crew providing actors and director with all the requisites and conditions they require for their outstanding performance. In the last decades genomics (director) and proteomics (actors) have been rightly standing very much in the scientific spotlight, providing a tremendous boost in these areas that has resulted in ground breaking genomic toolsets enabling mankind to sequence genomes in a couple of weeks to months and proteomics applications and technology that allow scientists to identify even the tiniest amounts of proteins present in a cell. The information output of these experiments is without doubt invaluable and has set an indispensable basis for various biosciences. Nevertheless, it has become more evident that knowing who is directing and playing the lead does not result in knowing and understanding the plot. So looking at the bigger picture on how cells communicate, how cells interact and what distinguishes „good" cells from „bad" ones requires tools that provide us with the means that not only tell us who is acting and directing but what the costume, make up and script of the actors look like.

Protein Function Fine Tuning by PTMs

One of the cell's most important costume and makeup artists are the protein Post Translational Modifications (PTMs) such as phosphorylation and glycosylation. These PTMs are frequently used by nature to influence the biological activity of proteins and endow them with additional functions. Phosphorylation is mostly found on intracellular proteins, whereas various different types of glycosylation are the common modifications found outside the cell on secreted and membrane proteins. More than 50% of human proteins are predicted to be glycosylated **[1]**, however knowledge on the type of glycosylation and its impact on the biological activity of particular glycoproteins is still restricted due to the great heterogeneity of glycoproteins, their involvement in diverse biological events and the lack of adequate methods for high throughput glycoproteomics screening that simultaneously includes both parts of the glycoprotein – the peptide AND its glycosylation.

Glycoproteomics requires interdisciplinary interaction between glycomics and proteomics

Understanding the intra and inter-cell biological protein functions requires sophisticated and novel tools and means for identifying and characterising PTMs and their location on the proteins. In principle, glycoproteomics is subdivided in three categories (**Fig. 1**) **[2]**: glycoprotein focused glycoproteomics is targeting the concomitant identification of both aspects of glycoproteins, their protein backbone as well as their glycosylation and in the best case also providing site specific structural information on the glycans present on a particular site. This glycoprotein focused approach provides the maximum in information, however is currently more constrained to bottom up analyses rather than top down approaches due to the limitations of available software and almost exponentially increasing complexity of analysing peptides including their glycosylation.

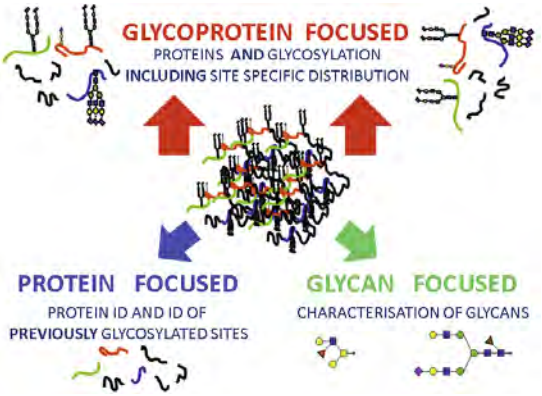

Fig. 1: Variations of Glycoproteomics. The glycoprotein focused approach targets at obtaining the most comprehensive information from glycoproteins and is supported by the protein and the glycan focused approaches.

PGC LC ESI MS/MS Glycomics

Porous Graphitized Carbon (PGC) LC ESI MS/MS provides the perfect basis that allows development of a ground breaking platform for simultaneous qualitative and quantitative glycomics. Current technologies are limited with regard to accurate absolute quantitation and/or appropriate glycan isomer identification and quantitation. The work in this project, however, will take high throughput PGC LC ESI MS/MS, to a completely novel and never before seen level of accuracy for both, qualitative and quantitative glycomics. One of several reasons making PGC LC ESI MS/MS the method of choice is its supreme power of separating so called isobaric glycan isoforms, structures that have the same mass but differ in the way the monosaccharide building blocks are linked together (**Fig. 2**) **[3]**. Exact and distinct differentiation of altered linkages is however crucial when dealing with glycoproteins since these differences are one of nature's opportunities for altering biomessaging pathways. Thus understanding glycoprotein functions and how e.g. cell-cell interactions are regulated requires efficient, sensitive and high throughput ways of differentiating exactly these structural features and is best done using released glycans.

Glycoproteins – Promising Biomarkers

Glycosylation has been shown to have tissue specific characteristics and reflect changes in various diseases particularly in cancer and inflammation **[4]**. Various proteomics studies on tissue and/or plasma often report differences between healthy and disease states at the protein level **[4, 5]**, however unless a tissue or disease specific protein is identified (e.g. prostate specific antigen [PSA], itself a glycoprotein **[6]**), single protein biomarkers alone often lack specificity and do not allow for unambiguous conclusions about a disease and its progression. Exploiting concomitantly both the glycan AND protein aspect of glycoproteins as diagnostic markers promises more specificity and sensitivity **[7, 8]** and will improve diagnosis and monitoring of diseases. Furthermore, an integrated approach investigating both aspects of glycoproteins will also lead to better understanding of biological processes and may result in identification of unique signatures for certain diseases.

Glycoproteins and Inflammatory Bowel Diseases

Crohn's disease and ulcerative colitis are chronic inflammatory diseases resulting from an inappropriate immune response to microbial antigens of commensal microorganisms. This inappropriate response is promoted by certain environmental factors, genetic predisposition, nutrition, environment and ethnicity. Both diseases manifest themselves primarily in the gastrointestinal tract yet can, in principle, affect all of the organ systems of the body. More than 300 000 people in Germany alone suffer from IBD. The incidence and prevalence of IBD have risen in the past 10 years, particularly for Crohn's disease with every fifth IBD patient being a child or adolescent. IBD is also associated with an increased risk of colorectal cancer, which itself is already the third most common cancer in developed countries. A cure of IBD is still not possible, yet the opportunities for diagnosis and treatment did show some improvement in recent years **[9]**. Early diagnosis is important so that patients can be referred onward for further diagnostic evaluation and appropriate treatment without delay. Nevertheless, the exact causes and triggers are still not well understood and efficient and specific biomarkers are still not well developed. There are several independent studies showing the connection between lectin and toll like receptors in autoimmune diseases **[10, 11]**. The finding of a variety of antibodies directed against different bacterial glycans is one of the latest approaches for diagnosing IBD **[9]**, however these approaches focus on the body's immunological reaction rather than the actual events occurring in the affected tissue. These previous findings strongly substantiate the significance of approaching IBDs and auto immune diseases from a glycoproteomics perspective. Understanding IBD initiation and development will help improving diagnosis, monitoring and treatment of IBDs as well as increase the understanding of factors leading to the progression to bowel cancer.

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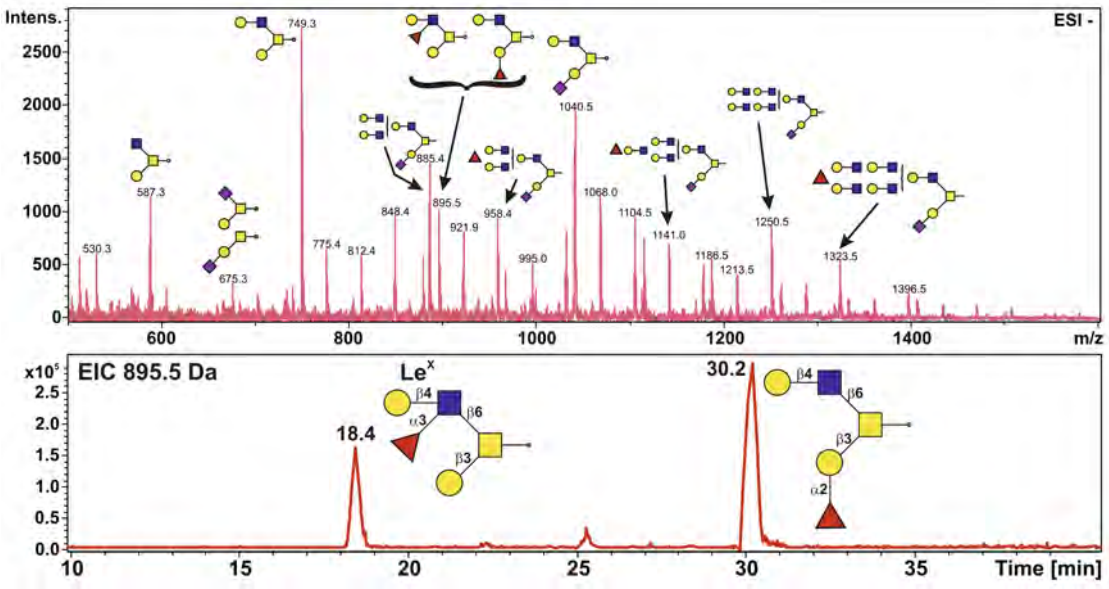

Fig. 2: Glycan isomer separation on PGC. Top: Mass spectrum summed from 16-35 min giving an overview of different glycan compositions present. Bottom: Extracted Ion Chromatogram (EIC) of m/z 895.5 corresponding to the singly charged O-glycan pentasaccharide. The difference of the fucose linkage and position results in significantly different retention times allowing separate analysis and thus clear distinction by MS of these isobaric glycan isomers. (modified from Kolarich D, Jensen PH, Cheah WY, Grinyer J, Packer NP, Protein glycosylation of human breast milk: an antimicrobial defense mechanism, manuscript in preparation)

Solid Phase Polymer Synthesis

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Thesis: Modification of enzymes by covalent attachment of poly(oxazolines)
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Thesis: Synthesis of monodisperse, multifunctional poly(amidoamines) and their application as non-viral vectors for gene therapy
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Introduction

Over the past decades, polymer-based materials have evolved as a powerful tool in biomedical and pharmacological applications. Designing a suitable polymer-based material for a specific biomedical application starts with the choice of monomer, but the crucial building block of material design is the homopolymer chain. The choice of chain length, geometry and the ability to couple different homopolymer chains influences the resulting morphology and chemical and biological properties, e.g. through the self-organization of block copolymers. In contrast to this approach, nature is able to control material properties using much smaller building blocks. The most dominant example is the primary sequence of proteins. Such molecular precision and advanced functionality is not yet possible for artificial polymer-based materials. Combining Nature's elegant approach with the existing possibilities of polymer nanotechnology, it seems feasible to achieve new generations of highly functional well defined polymeric materials. Therefore, the central focus of our work is the design and implementation of new synthetic strategies towards sequence-defined, monodisperse polymers using solid phase polymer synthesis.**[1, 2]**

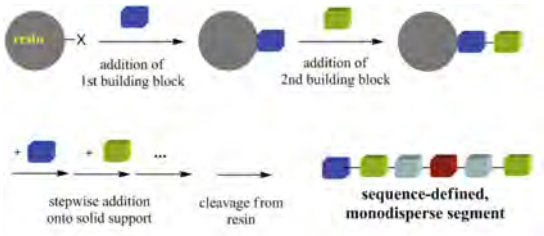

Fig. 1: General scheme for solid phase polymer synthesis. The stepwise addition of building blocks allows for the control over chain length and the positioning of different functionalities within the polymer chain.

In order to develop a straightforward synthetic route to sequence-defined, monodisperse polymer segments, a solid phase-supported synthesis strategy was applied (**Fig. 1**). The approach is based on the classical Merrifield solid phase peptide synthesis (SPPS). In theory, the carefully controlled stepwise addition of building blocks should provide polymer segments of a defined length with no molecular weight distribution. For every addition, a different building block can be used, introducing different functionalities within the chain depending on the choice of the monomer sequence.

Building Blocks for Solid Phase Polymer Synthesis

The choice of monomeric building blocks depends on a set of prerequisites: In order to maximize the flexibility and minimize the synthetic complexity for building block design, two different approaches are suitable (**Fig. 2**): 1.) The coupling of diacid and diamine building blocks allows for the formation of the polyamide backbone without the use of protecting groups.**[3]** 2.) Alternatively, a dimer building block can be used. This dimer is synthesized by condensing a diamine and diacid building block prior to solid phase coupling. In this case, an additional Fmoc-protecting group on the amine group must be introduced to avoid side reactions.

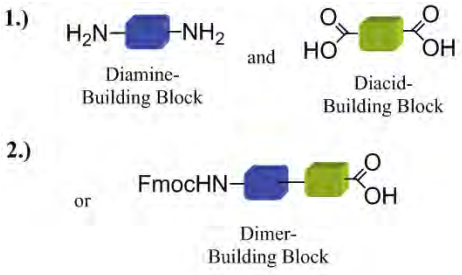

Fig. 2: Building blocks suitable for solid phase polymer synthesis can be either diamine and diacid building blocks (1.) or dimer-building blocks (2.) comprising a Fmoc-protected amine group on one side and a carboxylic functionality on the other side of the repeating unit.

In both cases, additional functionalities can be incorporated into the side chains for each monomer. Depending on the desired functionality, additional protecting groups may be required.**[4, 5]** In the ideal case each coupling will proceed with complete fidelity to avoid formation of side products and deletion sequences, thus eliminating the need for chromatographic separation after the final cleavage. Automated synthesis using a standard peptide synthesizer is of particular interest, since these systems have proven fast, efficient and reliable for generating defined polymeric structures. For this reason, the building blocks used on the synthesizer must be compatible with the reaction conditions suitable for automation such as chemical stability at room temperature, solubility in DMF or NMP and fast coupling reactions.

Introducing Functionality through Building Block Design

Taking the general concept of diamine and diacid or dimer building blocks, different functionalities can be introduced either in the polymer backbone or in the side chain. So far four different classes of building blocks have been established (**Fig. 3**).

The first class of building blocks (**Fig. 3**, A and B) are the functional building blocks. They introduce additional functionality for further modifications. Here, two examples are presented: The introduction of alloc-protected amines allows for modification of the building block following standard peptide coupling protocols (**Fig. 3 A**). Alternatively, the introduction of an alkyne group facilitates the use of click chemistry e.g. to attach azide-functionalized moieties (**Fig. 3 B**). These functionalities are of particular interest since they have been used to couple biologically active molecules such as monosaccharides. (**Fig. 3, C and D**). Another class of building blocks, known as charged building blocks (**Fig. 3, E and F**) focuses on the introduction of different charges such as cationic amine functionalities or anionic sulfate groups. Here, protecting groups are necessary to maintain solubility and avoid undesired side reactions during the solid phase coupling process. The fourth class of building blocks introduces chirality to the building block design (**Fig. 3, G and H**). Chiral building blocks will help to further control the structure of the polymer segment. For example, they can induce formation of secondary structures such as helices through stereo-controlled intramolecular interactions.

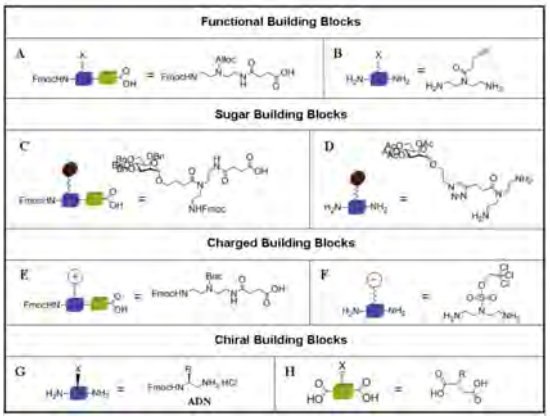

Fig. 3: Building Block Alphabet. Several building blocks suitable for solid phase polymer synthesis are shown. Functional building blocks allow for the modification through additional reactions steps e.g. by peptide chemistry or click chemistry (A and B). One important example thereof is the attachment of sugar moieties to the building blocks (C and D). Charged building blocks allow for the precise positioning of different charges within the polymer chain such as cationic amine groups or anionic sulfate groups (E and F). In order to control the structure of the polymeric backbone, chiral diamine and diacid building blocks have been introduced (G and H).[6]

An Example: Introducing Chirality to Monodisperse Poly(amidoamine)s

In order to obtain chiral building blocks suitable for solid phase synthesis, we introduced a synthetic strategy using a natural amino acid as starting material for the synthesis of a mono Fmoc-protected diamine building block. In a six-step synthesis starting from Boc-L-alanine, the chiral building block ADN was obtained in high yields and on a multi-gramm scale sufficient for solid phase synthesis.**[6]** Applying standard automated polymer synthesis protocols, the first polyamide oligomer was synthesized using succinic anhydride (Suc) as the diacid and ADN as the diamine building block. After addition of 4 repeating units, the final product NH_2-(Suc-ADN)$_4$-NHFmoc was cleaved off the resin and isolated by precipitation from Et_2O. Analysis by MS and HPLC confirmed the monodispersity of the final oligomer and the absence of any deletion sequence or undesired side products (**Fig. 4**).

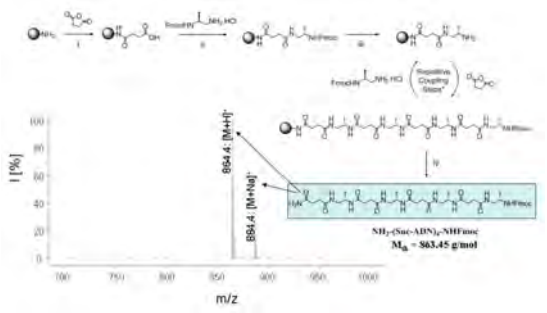

Fig. 4: Synthesis and analysis of the first poly(amidoamine) segment introducing chiral centers. The ESI-MS spectrum shows the signal for the monodisperse polymer segment and proves the absence of any side products or deletion sequences.

Outlook:

There is great potential for highly defined polymer systems with no molecular weight distribution and offering control over the monomer sequence. Our future work in this area will focus on expanding the repertoire of building blocks that can be used to generate polymers with different functional moieties and structural morphologies. These systems will be of particular interest for biomedical applications as they will serve as tools to study the direct correlation between the monomer sequence and the resulting chemical and biological properties. This will help to further understand the interactions of fully synthetic systems with biological systems and to use these interactions for the design of bioactive polymer-based materials.

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Synthetic Carbohydrate Vaccines

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Vaccines are efficient and cost-effective means for the global prevention of diseases. Carbohydrate antigens presented on the surface of disease causing pathogens have the potential to serve as vaccines. Candidates for carbohydrate based vaccines against cancer, viruses, bacteria and parasites form the focal point of research **[1, 2]**. Our department follows a comprehensive approach to synthetic carbohydrate vaccine development, starting from the synthesis of novel carbohydrate building blocks, to the generation of complex carbohydrate antigens, followed by conjugation to carrier-proteins and immunological evaluation including *in vivo* challenge studies.

Carbohydrate Antigens from Bacteria and Parasites

Carbohydrate structures of bacteria and parasites often differ significantly from mammalian structures and are recognized by the mammalian immune system. Carbohydrate-based vaccines against several bacterial pathogens such as *Neisseria meningitides, Streptococcus pneumoniae*, and *Salmonella typhi* are marketed. These vaccines are typically composed of purified carbohydrates isolated from the respective pathogen. The isolation of carbohydrates from cultured bacteria, however, often yields scarce amounts of heterogeneous oligosaccharide mixtures. Furthermore, only a small number of bacteria can be cultured in the laboratory. The synthesis of carbohydrates on the other hand gives access to large quantities of pure, well-defined carbohydrates.

Synthetic Carbohydrates

Automated oligosaccharide synthesis pioneered by our department is a powerful tool for the synthesis of carbohydrate antigens, as it allows for the rapid assembly of complex oligosaccharides. The targeted carbohydrate antigens are oligosaccharides composed of monosaccharide units. Most monosaccharide building blocks are readily accessed by modification of commercially available sugars. Some monosaccharides, specific to certain bacteria, are only accessible via *de novo* synthesis. One particular monosaccharide, 2-acetamido-4-amino-2,4,6-trideoxy-D-galactose (AAT) is a component of zwitterionic polysaccharides (ZPSs) found on the cell surface of some pathogenic bacteria. ZPSs are of particular interest as they induce a T-cell-dependent immune response. AAT building block 2 (**Fig. 1**), synthesized in less than twelve steps from *N*-Cbz-L-threonine 1, was used to construct disaccharide 3, a fragment of the repeating unit of polysaccharide A1 (PS A1) 4 found in *Bacteroides fragilis* **[3]**. The first total synthesis of the PS A1 repeating unit 4 **[4]** was then performed starting from 3. PS A1 repeating unit 4 is currently being used to develop immunological probes for *B. fragilis*, which hopefully will help unravel the mechanism and action of zwitterionic PS A1.

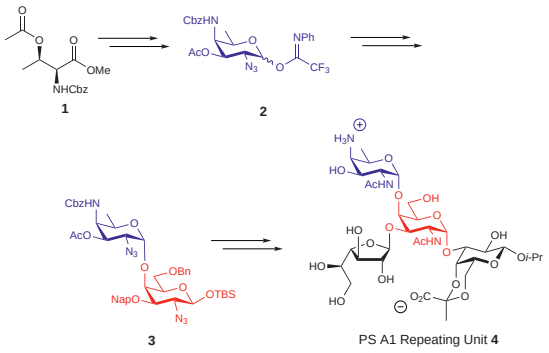

Fig. 1: Total synthesis of the repeating unit of the zwitterionic polysaccharide A1 4 from B. fragilis, via the AAT-containing disaccharide 3.

From Synthetic Carbohydrates to Vaccines

Carbohydrates are generally T-cell-independent antigens that neither promote immunoglobulin class switching from IgM to IgG nor memory responses, crucial for long-lasting protection. For this reason, carbohydrate antigens are covalently linked to carrier proteins. This leads to carbohydrate-specific antibody production and memory cells with carbohydrate based vaccines then eliciting long-lasting protection. The immune response can further be enhanced by the use of adjuvants.

Tools for Studying Carbohydrate Antigen-Antibody Interactions

A central element for understanding the mechanism of vaccines requires developing an understanding of the underlying antigen-antibody interactions. These are investigated by enzyme-linked immunosorbent assay (ELISA), glycan microarrays, surface plasmon resonance (SPR) and saturation transfer difference (STD) NMR.

Glycan microarrays consist of carbohydrates immobilized on surfaces in high density and spatially defined manner. They can be employed as diagnostic tools for the detection of anti-carbohydrate antibodies **[2]**. Glycosylphosphatidylinositol (GPI) microarrays were recently used to determine the specificity of anti-GPI antibodies for a synthetic GPI from *Plasmodium falciparum* in healthy and malaria diseased individuals **[5]**.

The synthetic tetrasaccharide component of the glycoprotein Bc1A of *Bacillus anthraxis* is immunogenic in mice, leading to the production of antibodies. Quantification of the tetrasaccharide-antibody interaction confirmed the tight binding previously observed with glycan microarrays. Furthermore, the tetrasaccharide-antibody pair was subjected to STD NMR experiments, which give insight in crucial binding elements of the antibody-binding surface of the carbohydrate antigen on atomic level (**Fig. 2**) **[6]**.

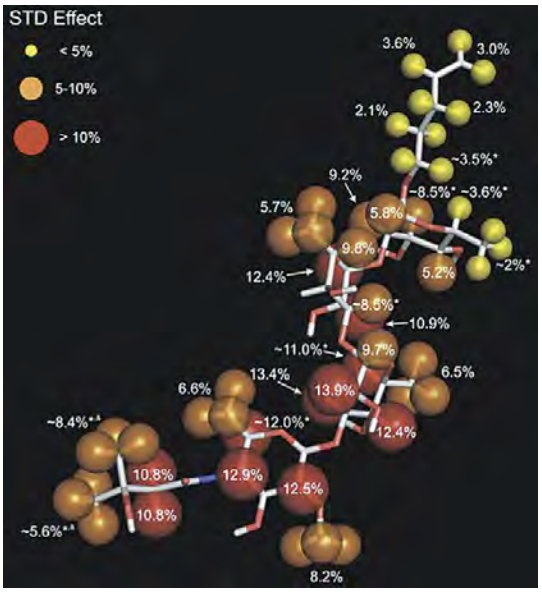

Fig. 2: Epitope mapping of the tetrasaccharide-antibody interaction by STD NMR. Percent STD effects are shown for individual protons of the tetrasaccharide.

The Future of Synthetic Carbohydrate Vaccines

Most carbohydrate-based vaccines on the market still contain purified carbohydrates isolated from biological material; this is due to the lack of accessibility to large amounts of synthetic carbohydrates. Automated oligosaccharide synthesis could help overcome this bottleneck, giving a significant boost to synthetic carbohydrate vaccines.

At the moment we are investigating a number of synthetic carbohydrate vaccine candidates, ranging from pathogens responsible for a large number of casualties in developing countries, to antibiotic resistant bacteria, typically found in hospitals of developed countries.

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Continuous Flow Reactors as Tools for Organic Chemists

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Our department has pioneered the use of continuous flow reactors by synthetic organic chemists. Continuous flow reactor systems offer significant advantages when performing reactions which are mixing controlled, or where heat- and mass-transfer are important. These properties derive from the exceptionally high surface-to-volume ratios accessible in continuous flow reactors. It is simple to scale-up microreactor processes either by numbering-up reactors or running the reaction for extended duration. We utilize both commercially available and internally developed systems (**Fig. 1**), ranging from microliter-volume etched silicon chips to milliliter-volume tubing reactors. Our work with these systems has exemplified the broad scope of their application, not only in traditional organic chemistry, but also in the preparation of polymers, nanoparticles and functionalized biomolecules.

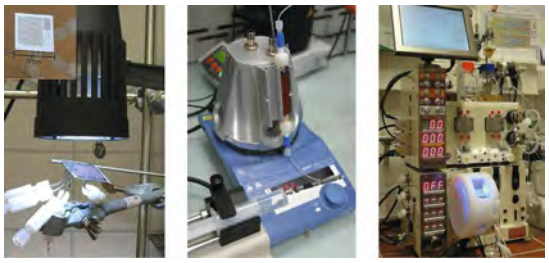

Fig. 1: Microreactor systems in our department (from left): 78.6 μL silicon chip under irradiation using an LED light and (inset) detailed view of the reactor chip; a packable column for the continuous flow use of solid reagents and catalysts; HPLC pump-driven Vapourtec R-Series system fitted with 10 mL cooled reactor.

Reactions of Hazardous and High-Energy Species

Continuous flow reactor systems provide ideal conditions for the detailed study of the formation and subsequent transformations of high-energy compounds. High temperature and pressure conditions can be achieved with improved safety and efficiency compared to batch processes; superheating of solvents is simple and hazardous reagents can be more safely handled by minimizing their concentration at the point of reaction. Additionally, the short residence times accessible in microreactors often reduce the potential for side reactions of highly reactive species. In addition to safe and efficient amidations of esters using pyrophoric $AlMe_3$ **[1]**, radical reductions **[2]** and fluorinations with the thermally-unstable fluorinating agent DAST **[3]**, we have studied the continuous flow generation of nitrenes *via* thermolysis of azides **[4]**. Continuous flow thermolysis of 3-aryl-2-azidoacrylates to give indole 2-carboxylates, previously requiring sealed tube conditions and extended heating of potentially explosive azides, has been successfully performed in our laboratory (**Fig. 2**). We applied this method to the synthesis of a variety of heterocycles, with exceptionally high productivity.

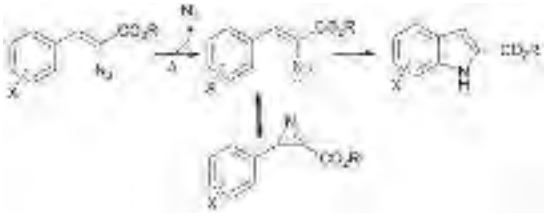

Fig. 2: Continuous flow thermolysis of azidoacrylates to give indole-2-carboxylates.

Polymers

Classical emulsion polymerization produces high molecular weight polymers at high rates of polymerization, rendering this process very attractive for industrial applications. Recent improvements in the regulation of reaction conditions, safety and quality control have prompted efforts toward miniaturization, embracing advances in microfluidics. In collaboration with the MPIKG Colloid Department and the ETH Zürich, we have developed a continuous flow emulsion polymerization process using phosphine oxide photoinitiators **[5]**. Polymer nanoparticles of very high molecular weights were formed by a novel mechanism (**Fig. 3**). Incorporation of phosphine oxide units into the polymer backbone induces repeated, snowballing radical generation upon irradiation where polymer-associated mono- and diradicals are created and do not terminate instantly. This process dramatically increases the radical polymerization rate and generates long polymer chains with ultrahigh molecular weights. The avalanche-like formation of radicals that occurs inside the latex particle also causes an enormous increase in the average number of growing polymer chains per particle. A stochastic model was used to simulate snowballing kinetics and quantitatively rationalize the polymerization process.

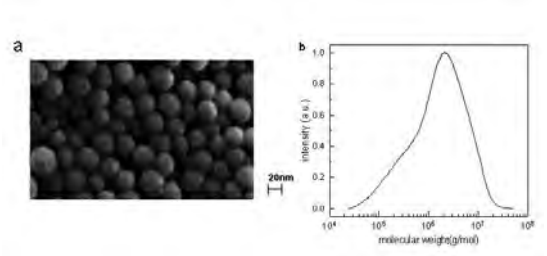

Fig. 3: a) SEM image of polystyrene, b) Molecular weight distribution of the polystyrene chains produced via photoinitiated emulsion polymerization.

Controlled free radical polymerizations (CRP) have evolved over the last 20 years into very useful and widely applied techniques for polymer synthesis, combining the excellent control of traditional ionic living polymerizations with robust conventional free radical polymerizations. Among these techniques, reversible addition fragmentation chain transfer (RAFT) represents the most versatile and facile method. In contrast to generally fast free radical polymerizations, the controlled living process requires longer reaction times.

Heating by microwave irradiation can considerably shorten the reaction times, but the scale-up of microwave reactions is difficult. We developed the first homogeneous RAFT polymerizations in a continuous flow reactor **[6]**. The polymerization is considerably faster when compared to batch reactions (**Fig. 4**). Thermoresponsive PNIPAM with apparent molecular weight of 20 kDa was obtained within minutes in flow, instead of hours in batch. The continuous flow polymerization exhibited similar kinetics as under microwave irradiation, but with the advantage of being readily scalable.

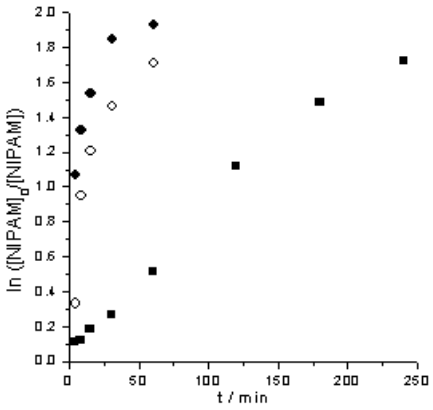

Fig. 4: Pseudo first-order plots of the polymerization at 90 °C and n = 200 in batch with conventional heating (■), microwave irradiation (●), and conventional heating in continuous flow (○).

Nanomaterials

The need for large quantities of monodisperse semiconductor nanocrystrals, (quantum dots – QDs), and the difficulty of their preparation via traditional batch techniques has prompted us to explore the use of continuous flow microreactors **[7]**. Taking advantage of the precise temperature control and efficient heat transfer of continuous flow microreactors allowed reduction of the reaction temperature from 300° C to 160° C. Lower temperature prevented the fast nucleation and generation of large non-homogeneous nanocrystals. By varying the residence time between 3 and 30 minutes, different sized CdSe and CdTe nanoparticles were obtained. The different size leads to different physical properties, especially the luminescence maxima (**Fig. 5**). Characterization of the different QDs by transmission electron microscopy (TEM) revealed highly crystalline, monodisperse, cubic nanoparticles. A microreactor was also used for the preparation of carbohydrate-functionalized QDs under mild liquid-phase conditions for the investigation of specific carbohydrate-lectin interactions.

Functionalization of Biomolecules

Dendronized polymers are multivalent, flexible systems that can bend to adapt to the environment of a pathogen surface and optimize binding to bacterial carbohydrate receptors. Functionalization of these polymers is challenging as the coupling reaction must be selective and high yielding, whilst not contaminating the end product. To address this challenge, we

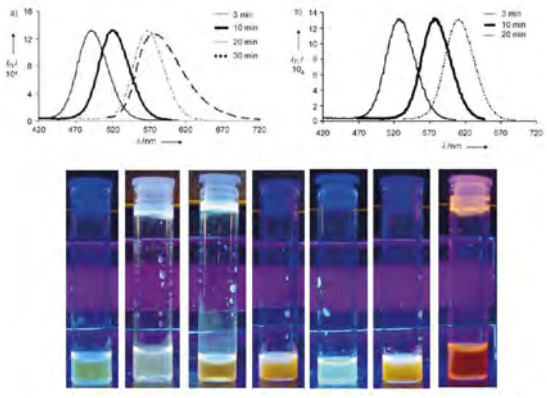

Fig. 5: Normalized luminescence spectra of a) CdSe nanoparticles in chloroform after 3, 10, 20, 30 min, and b) CdTe nanoparticles in chloroform after 3, 10, 20 min.

explored the usefulness of photochemical [2+2] cycloaddition, which can be carried out in water using inexpensive starting materials; it is pH independent and circumvented the use of heavy metals or other reagents that contaminate the polymer product **[8]**. Traditionally, photochemical reactions have been poorly scalable. Using a continuous flow photochemical reactor allowed us to develop an efficient, fast and readily scalable synthetic route to dendronized polymers. We are continuing to investigate the continuous flow conjugation of biomolecules with carbohydrates.

Reaction Optimization and System Development

In both industrial and academic settings, much of the effort spent by synthetic organic chemists is consumed searching for optimal reaction conditions to achieve a particular transformation. A key advantage to performing chemistry in microreactor systems is the speed with which mechanistic data can be obtained and conditions altered. Thus, only small quantities of reagent are required for the optimization process. We have developed screening platforms for the systematic study of glycosylation reactions: a transformation of critical importance for our department **[9]**. By combining automated screening with inline analysis and design-of-experiment algorithms, we are now developing completely automated optimization systems. We work closely with industrial partners in this area, using our experience in continuous flow microreactor technology for rapid process development.

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Glycosylphosphatidylinositols

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GPI-Anchored Proteins

Many proteins and glycoproteins are attached to membranes by means of a glycolipid called Glycosylphosphatidylinositol (GPI). In Malaria infection, specific GPIs were found to act as toxin, nevertheless the divers biological role(s) of these glycolipids is still under investigation. GPIs are becoming recently of high interest in carbohydrate based vaccines and glycobiology.**[1, 2]** The structure of the GPI molecule is variable and species depending, however a conserved common core pentasaccharide has been observed (**Fig. 1**). These GPI conserved core pentasaccharide have been reported containing different modifications like phosphorylations, acylations and additional glycosylations. **[3]**

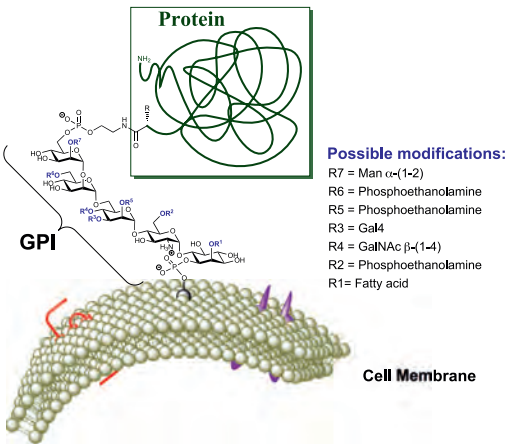

Fig. 1: Structure and modifications of the glycosylphosphatidylinositol (GPI) anchor.

An example of a GPI-anchored protein is the Prion protein (PrP), a protein known to be the infectious agent causing transmissible spongiform encephalopathies (TSEs). A secondary structural modification of the ubiquitous PrP to the infective form, called scrapie form (PrPsc) of the protein, increases the beta sheet conformation, which favored the aggregation of the protein and the generation of fibrils. The mechanism of this conformational transformation is still unclear; however recent studies have reported a faster spreading of this miss folding with the presence of the GPI-Anchor. **[4]**

In order to understand the role of the GPI in the conversion of PrP to PrPsc, in the pathogenesis of PrPsc and other different biological processes, the synthesis of uniform GPI units and GPI-anchored proteins is highly necessary.
Native chemical ligation (NCL) is actually the most extended method for the chemical synthesis of proteins, including proteins with posttranslational modifications.**[5]** This chemoselective reaction is based in a transthioesterification between a thioester and the thiol group of a cysteine residue following by an S→N acyl transfer to generate an irreversible new amide bond.

In a previous report of the Seeberger group **[6]**, an expressed PrP bound to a synthetic GPI unit with two phosphorylations was obtained by NCL. Although the GPI unit was not in its natural structure, the general feasibility of this strategy for obtaining GPI-anchored proteins was clearly demonstrated.

In order to obtain the natural GPI anchored PrP, the syntheses of the GPI unit have been improved and extended. The new general strategy allows now the incorporation of typical modifications found in mammalian GPI molecules as phosphorylation and branching in the Man 1 residue, lipidation and the cysteine residue required for the NCL (**Fig. 2**).

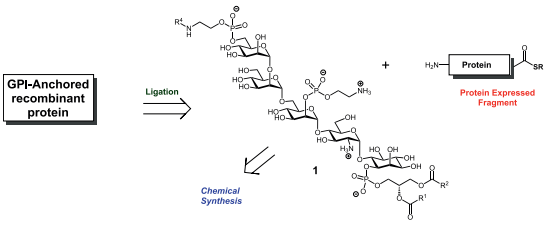

Fig. 2: General strategy for the synthesis of GPI-anchored proteins.

Synthesis of GPI Anchors

GPI molecules can been obtained by a modular strategy using different building blocks. The pseudo glycan part has been synthesized using a [2+1+2] glycosylation strategy with three building blocks (**Fig. 3**). After obtaining the building blocks, the efforts have been concentrated on two aspects of the synthesis: the introduction of three phosphorylations into the core glycan pentasaccharide using H-phosphonates and the synthesis of the branched glycan part (**Fig. 3**).

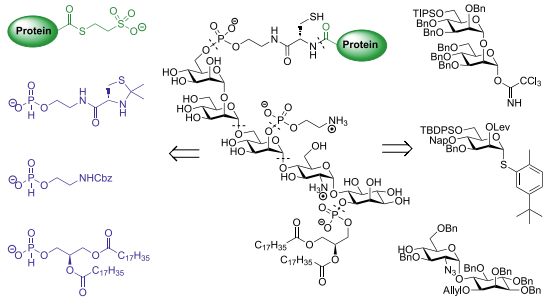

Fig. 3: Retrosynthetic analysis for the synthesis of GPI anchors.

A set of orthogonal protecting group was introduced to perform three phosphorylations sequentially. Three H-phosphonates were pre-synthesized from phosphonic acid under known conditions **[7]**, a diacyl glycerol, a phosphoethanolamine and a cysteine containing block. The activation of the H-phosphonates was performed with pivaloyl chloride and good yields were obtained.

Using the strategy described synthesis of the first fully phosphorylated Prion GPI has been achieved. Furthermore the strategy for incorporation of the galactosamine branching has been optimized. The synthesized molecules are now being used for NCL to obtain GPI-anchored proteins. These steps are currently performed and manuscripts summarizing these latest results are prepared for submission to well recognized journals.

The challenge of introducing the branching glycosylation found on the GPI of PrP and other mammalian GPIs was achieved by using the napthyl protecting group present in the strategy. This approach allowed us to obtain the core pseudopentasaccharide. The protecting group can be removed selectively using oxidative conditions. The pre-synthesized building blocks can be bound using different glycosylation strategies resulting in the desired GPI pseudo glycan structures before introducing the phosphorylations. This methodology enabled the elongation of the GPI glycan moiety with different branched structures up to a heptasaccharide. The availability of these synthetic GPIs builds the basis for the continuing with the next steps for synthesizing GPI anchored PrP and other proteins containing different carbohydrate structures. In future this will allow us to evaluate the biological role of GPI structures.

Synthesis of Homogeneous Glycoproteins

Glycoproteins are involved in diverse biological events like fertilization, neuronal development, hormonal regulation and immune and inflammatory responses. However, the influence of particular glycoprotein carbohydrate structures on these processes is still largely unknown.**[8]**

Glycoproteins are naturally present as a mixture of so-called glycoforms, (identic protein sequence with different glycosylation patterns), making the determination of the carbohydrate role in protein function challenging.

The synthesis of uniform glycoproteins has recently emerged as a promising alternative to overcome the essentially impossible isolation of single well-defined glycoforms. Native chemical ligation has developed as an appropriate method for chemical glycoprotein synthesis (**Fig. 4**). Chemically synthesized glycopeptides are coupled with recombinantly expressed protein fragments to result in a uniform glycoprotein. Although this strategy has allowed the synthesis of small proteins, new ligation methods and improvement of the fragment synthesis are required.

Using therapeutically used interferons (glycoproteins of the immune system) as a model, methods are currently developed to obtain uniform glycoproteins based on the chemical synthesis. Initial efforts are concentrated in glycopeptide solid phase synthesis followed by ligation coupling methods resulting in intact glycoproteins.

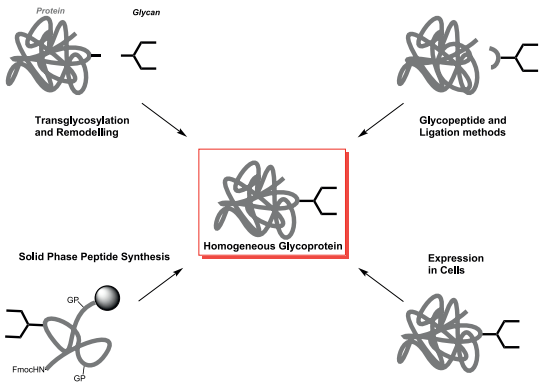

Fig. 4: Methods to obtain homogeneous glycoproteins.

First, a sialoglycopeptide undecasaccharide has been isolated from the delipidated fraction of egg yolk. The purification was performed by size exclusion chromatography and anion exchange chromatography. A glycosylated asparagines is obtained by enzymatic hydrolysis of the glycopeptide and can be selectively manipulated to obtain the protected building block for traditional Fmoc peptide synthesis.

In the second step, synthetic glycopeptides derived from the interferons alpha and beta will be converted to peptide thioesters or other active groups. These glycopeptides can then be submitted to ligation strategies with other peptides or coupled to expressed fragments resulting in well-defined glycoproteins.

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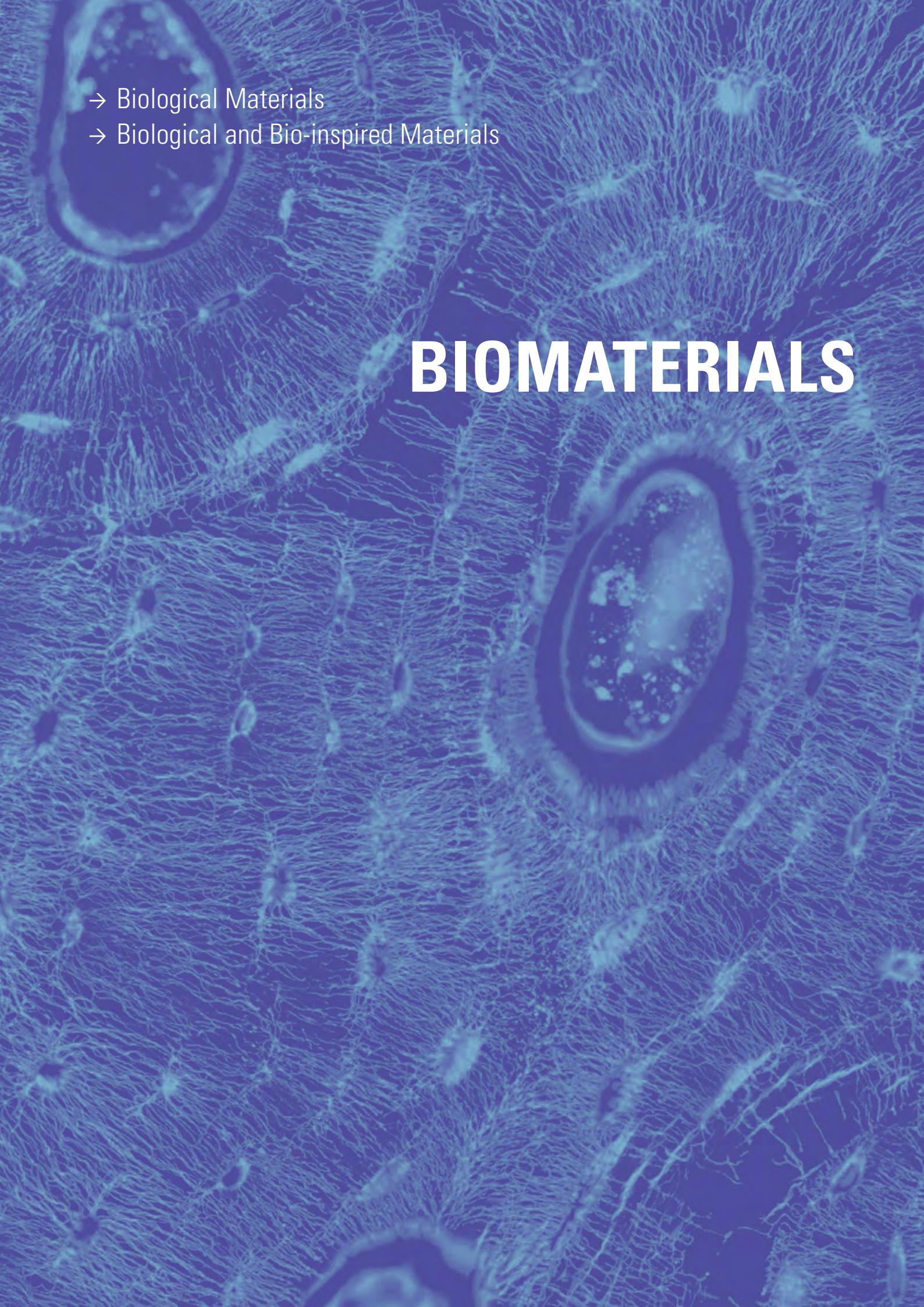
→ Biological Materials
→ Biological and Bio-inspired Materials

BIOMATERIALS



Research in the Department of Biomaterials

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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-Golm)
Since 2004: Honorary Professor of Physics at Humboldt University Berlin
Since 2009: Honorary Professor (Physics of Biomaterials) at the Potsdam University

Biological Materials Science is at the center of the research program in the Department of Biomaterials. This research is inherently multidisciplinary between physics, chemistry and biology, and its principle goals are:

- To use materials science approaches for studying structure-function relationships in biological systems, with potential applications in biology or medicine;
- To study the "engineering design" which arose during the evolution of natural materials and to extract useful principles for the development of new bio-inspired materials;
- To develop new materials for contact with biological tissues, leading to implantable biomaterials or with applications in tissue engineering.

All three areas are addressed in the Department; however, there is a significantly stronger emphasis on the first two. 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.

Structure of the Department

The Department is organized 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 a special methodology (such as synchrotron research or mathematical modeling). In this way, a strong expertise in a given field is maintained in each of the groups and important scientific problems at the interface between these disciplines are addressed by interaction and collaboration between them. Typically, the research groups encompass – in addition to the group leader – several doctoral students, postdocs, one or two technicians, as well as the responsibility for laboratories and the larger instrumentation of the institute. In addition to the research groups, several independent researchers, some of them with individual grants (e.g. from the Humboldt Foundation) work on chosen scientific projects, sometimes mentoring a student, but without responsibility for a larger group.

Methodological Approaches

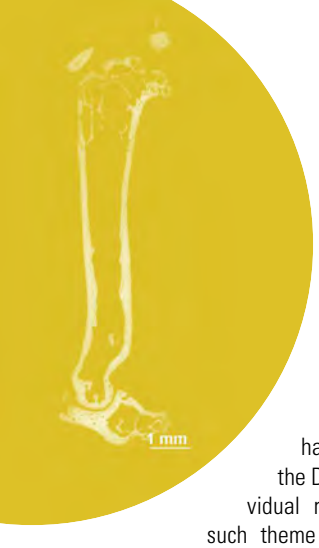
Generally, the experimental approach is based on multi-method imaging where different probes are used to image the same specimen. This provides information on different features of the materials such as micro-structure, chemical composition, or mechanical properties in a position-resolved manner with micron-range resolution . We are currently using x-ray tomography; scanning electron microscopy and scanning x-ray diffraction to characterize micro- and nanostructure (see, e.g. reports by *W. Wagermaier* and *P. Zaslansky*). We have established polarized and confocal Raman imaging to provide information on chemical composition and fiber orientation (see report by *A. Masic*), and we use nano-indentation as well as acoustic microscopy to estimate local mechanical properties. The strength of this multi-method approach is that the different parameters measured on the same specimen can be correlated at the local level with micron-scale spatial resolution. This facilitates the extraction of structure-property relationships even in extremely heterogeneous materials with hierarchical structure. Additionally, we are currently developing the infrastructure required to probe these materials at the biochemical level in order to better understand how specific molecular-level features of the biopolymeric building blocks influence bulk material properties (see report by *M. Harrington*).

In a second type of approach, we study *in situ* changes in various materials (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 which are responsible for the noteworthy properties of these materials. In some cases, such measurements 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 is operated at the synchrotron BESSY at the Helmholtz Zentrum Berlin (see report by *B. Aichmayer*).

These efforts are complemented by a significant effort in mathematical modeling, which is always closely tied to the experimental work in the department. Typically, modeling and experimentation go hand in hand with the research projects (see for example the reports by *J.W.C. Dunlop* and *R. Weinkamer*).

Visiting Scholars

Several experienced scientists have been spending significant time in the Department. *Franz Dieter Fischer*, professor of mechanics at the Montanuniversität Leoben (Austria) recipient of the Alexander von Humboldt Award, came for many short visits, which helped advance the mathematical modeling of tissue growth in particular (see report by *J.W.C. Dunlop*). *Hartmut Metzger* arrived in the beginning of 2010 from the European Synchrotron Radiation Facilities (ESRF), where he had been a staff scientist and group head responsible for several beamlines. He brought many years of experience in x-ray diffraction, in particular with grazing incidence and using coherent beams, to our Department. *Emil Zolotoyabko*, professor of materials science at the Technion (Israel Institute of Technology) spent several months of a sabbatical in the Department. He offered his general knowledge of materials science in many discussions, as well as an advanced course in crystallography, which was well attended by the scientists in the Department. In addition to developing new collaborations, our visiting scholars play an important role in the mentoring of young scientists, and we are most grateful to them for this very important contribution. Recently, it was announced that *Yves Bréchet*, professor of materials science at the Institut National Polytechnique de Grenoble (INPG) and at the Institut Universitaire de France (IUF) will receive the Gay Lussac-Humboldt Award to visit our Department in 2011.



Bone Research

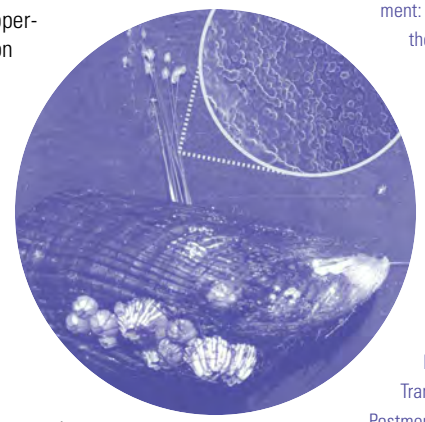
The director and the group leaders have defined overarching themes for the Department where many of the individual research groups collaborate. One such theme is bone research. The rationale behind these studies is that osteoporotic bone fractures, which have generally been associated with bone loss, may also be linked to changes (age- or disease-related) in the bone material itself. In collaboration with the Ludwig Boltzmann Institute of Osteology (Vienna, Austria), we study the changes in bone material quality in osteoporotic bone before and after treatment with various strategies. This is one area where we collaborate with industry, mostly in the framework of large clinical studies. Publications of the last two years addressed the effect on osteoporotic bone material following treatment with strontium ranelate. In particular, we showed that Sr is not only acting on the bone cells but gets incorporated into the mineral particles during treatment **[1, 2]**. Long-term treatment with the bisphosphonate alendronate, however, does not seem to affect the structure of the bone material significantly **[3]**. The adaptation of bone structure by the collaborative action of bone-forming and resorbing cells is modeled by the group of Richard Weinkamer. The importance of osteocytes, which are cells embedded in the bone matrix is studied within the framework of a BMBF consortium by the group of *Wolfgang Wagermaier* (see their reports and the references therein). Finally, the Department is very active in a consortium with the Charité Hospital Berlin (Julius Wolff Institute) and the Berlin-Brandenburg School of Regenerative Therapies, a graduate school financed by the German Science Foundation (DFG) through the excellence initiative. In this consortium, we study bone regeneration by characterizing and modeling the healing process, (see the reports by *Inderchand Manjubala* and by *Richard Weinkamer*) and explore routes towards bio-inspired tissue-engineering scaffolds **[4]** (see also report by *John W.C. Dunlop*).

Bio-Inspired Actuating Materials

Humidity-driven actuation plays an important role in plant movement, in seed dispersal and in the generation of growth stresses in trees **[5]**. We are studying natural systems where the material deformation is triggered by humidity as an external stimulus. The group of *Ingo Burgert* dedicates a large effort to this subject and additionally, we maintain a collaboration with *Rivka Elbaum*, a former postdoc in the Department and now at the Hebrew University (Israel). Numerical modeling of complex movements is addressed in the report by *John Dunlop*, with particular emphasis on the influence of the internal structure on deformation patterns. The report by *Matthew Harrington* shows the specific example of a desert plant seed capsule that opens upon contact with water droplets, despite consisting of non-living material. Recently, we started a more concentrated activity to investigate the interaction of water with deformable materials, in which we focus on wood fibres (see report by *Ingo Burgert*), as well as model material systems **[6]**. A new independent researcher, *Luca Bertinetti*, is starting to concentrate on these aspects.

Biomineralization

Two groups are focusing on issues related to biomineralization. *Damien Faivre*, who was just awarded an ERC Starting Grant from the European Research Council, works on elucidating how bacteria control the growth of magnetite nanoparticles through the interaction with specialized proteins. His group also addresses bio-inspired engineering problems in the context of nanorobotics and medical imaging with magnetic nanoparticles (see his report). *Barbara Aichmayer* leads a group working both on natural mineralized tissues (such as crayfish teeth) and on bio-inspired hybrid materials, based on polymers and mineral (see her report). She is also responsible for the operation of our synchrotron beamline MµSpot at the BESSY synchrotron of the Helmholtz Center Berlin. Together with the visiting scholar *Dieter Fischer*, we also model various aspects of biomineralization **[7]**.



Load-Bearing Natural Materials

Matthew Harrington is currently building a group focused on understanding the biochemical strategies utilized in load-bearing natural materials. In his report he describes the role of reversible metal coordination cross-links in the self-healing byssus fibres, which mussels use to attach to rocks. An essential component of these self-healing materials are sacrificial bonds, which have also been investigated theoretically **[8]**. In addition, several independent researchers report on their work on calcified cartilage in shark skeletons (*Mason Dean*), on structure–function relationships in the spider cuticle (*Yael Politi*), on Raman imaging of biological tissues, in particular collagen (*Admir Masic*) and on human teeth and dental restorations (*Paul Zaslansky*). Two of these independent researchers are financed by their own Humboldt Fellowships (*Dean* and *Politi*), and the remainder are supported by a Max Planck Research Prize, awarded to *Peter Fratzl* in 2008. The Gottfried Wilhelm Leibniz Prize 2010 will allow further increasing this research activity.

The majority of the research in the Department of Biomaterials involves collaborations – within the Department, with other Departments in the Institute and with many outside partners around the world who all deserve our sincere gratitude for cultivating and fostering such positive and constructive partnerships.

Peter Fratzl
Director of the Department of Biomaterials

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Bone Regeneration

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Regeneration of bone is a complex process involving both formation and resorption process. While bone is known to grow and heal itself, in some critical condition beyond the limit the bone formation is regulated by biochemical, mechanical and cellular mechanism. We focus on understanding the development of new bone formation under natural growth, fractured conditions and mimicked in-vitro conditions.

Tissue Formation under *in-vitro* Conditions by Osteoblast Cells

An *in-vitro* system in which the behaviour of tissue formation by the osteoblast cells (MC3T3-E1) in defined geometries can be monitored in real time was established with a standard hydroxyapatite material. Since material properties of scaffolds like surface topography, stiffness and geometry play a vital role in cell survival and their responses, linear copolymer polyether urethanes with different stiffness were used as three dimensional scaffolds. These scaffolds were provided by our SFB 760 project partner, Andreas Lendlein, GKSS Institute for Polymer Research in Teltow. It was observed that the cells do respond differently in different seeding conditions, depicting different delay times of tissue formation on these polymer scaffolds (**Fig 1a**) and more interestingly the tissue formation kinetics showed a two stage behavior wherein the late stage was similar to that of hydroxyapatite scaffolds (**Fig 1b**) **[1]**.

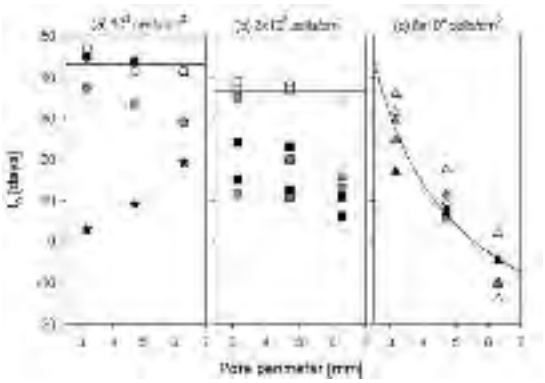

Fig. 1a: Delay time (t0) plotted as a function of pore size (perimeter). White, grey and black points represents polymer with different stiffness and star represents standard hydroxyapatite scaffold.

Apart from stiffness, the cells do respond to growth factors such bone morphogenetic proteins, BMP-2. But the responses of the BMP-2 on tissue formation are still not known and this task was carried out in cooperation with Petra Knaus, Freie University, Berlin. The continuous BMP-2 application increased proliferation and differentiation of pre-osteoblastic MC3T3-E1 cells. These observations made are of direct use in the optimization of scaffold design and has been the focus of a doctoral work **[2]**.

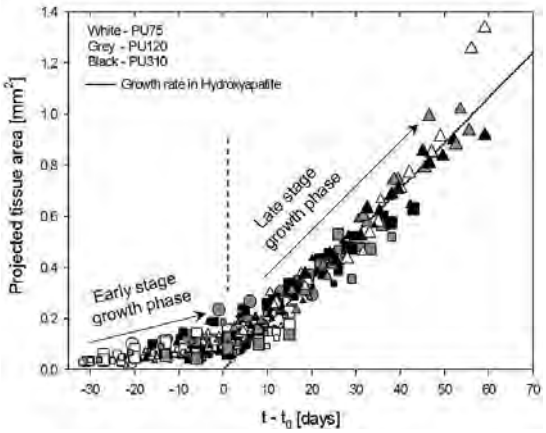

Fig. 1b: Normalized PTA data showing two stages of tissue growth in polymeric scaffolds.

Bone Healing and Regeneration

When bone is injured, a callus is formed enveloping the fracture site and is eventually remodeled back into bone to fully restore the initial morphology and function of the skeleton. While the histological evaluations describe the spatial and temporal distribution of the various tissue types comprising the callus, it is of vital importance to evaluate and understand local variations in callus material properties at the micro- and nano-scale. The investigation of the spatial distribution and temporal sequence of ultra-structural and mechanical properties of callus tissues over the course of healing has been the focus of a doctoral work **[3]**. This project is in cooperation with Georg Duda and colleagues, at Julius Wolff Institute, Charité-Universitätsmedizin Berlin where the bone healing experiments is carried out both in small and large animal models.

Measurements on similar regions of the same samples, with nanoindentation, scanning small angle X-ray scattering (SAXS) together with environmental scanning electron microscopy (ESEM) revealed the heterogeneous local mechanical property, size and orientation of bone mineral particles within the regenerating callus tissues **[4, 5]**. Both studies showed that the callus formation is characterized by two waves of bone formation. Starting from the periosteal region, a structurally disordered and mechanically inferior woven tissue was deposited first and replaced later by more

lamellar-like tissues with thicker and more aligned mineral particles, lower mineralization heterogeneity and higher mechanical competence (**Fig 2**).

In light of such findings, the X-ray study was extended from laboratory resolution to synchrotron resolution and from 2D to 3D. The simple but effective representation of 3D SAXS data and the reconstruction of 3D SAXS patterns enable a direct visualization of mineral alignment in the investigated sample volume, which provides insight into the 3D structural properties of the callus material as well as their relation with its mechanical performance **[6]**.

Bone regeneration and remodelling in other cases such as treatment with a stainless steel implant **[7]** or with a drug for osteoporosis **[8]** was also studied.

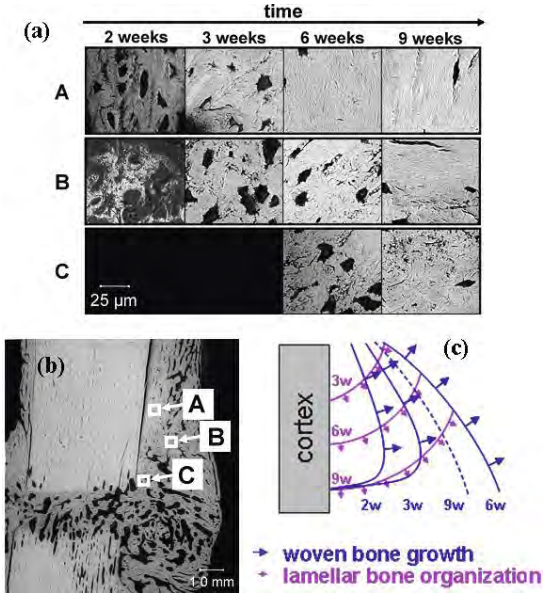

Fig. 2: (a) Back-scattered electron images (4000×) at three different locations, A, B and C with the callus as shown in the overview image (b). Different tissue types are visible: (i) an unmineralized fibrous tissue as observed in C at 2 and 3 weeks, (ii) a mineralized but poorly organized woven tissue as observed in A and B at 2 weeks and (iii) mostly lamellar bone as observed in A at 9 weeks. (c) It is proposed that the transformation from structure (i) to (ii) and from (ii) to (iii) occurs in two sequential "waves" propagating along the cortex towards the osteotomy gap.

Bone Growth and Development

The understanding of the mineralization process in vertebrates is of substantial interest since less is known about how mineral crystals nucleate, grow and organize themselves from the beginning of bone development and the question of the first-formed mineral phase is still controversially discussed. This study is a part of BSRT graduate school in Berlin, in cooperation with Stefan Mundlos, MPIMG. Using scanning small angle X-ray scattering technique at lab source as well as using microbeam line at BESSY, several remarkable results were obtained such as strong differences in shape and arrangement of the mineral particles between fetal and postnatal bone, indicating two different types of bone tissue. (i) Fetal bone tissue is characterized by spotty mineralization, short but relatively thick mineral crystals and no preferred orientation of the minerals, and (ii) the postnatal bone tissue can be described by continuous mineralization, long and slender crystals where length and thickness increase simultaneously with age and highly oriented minerals. This further confirms that possibly there is a strong change in tissue organization at birth and maybe not all calcium is bound in crystalline HA in fetal bone, possibly indicating the formation of a precursor phase of HA during early bone development.

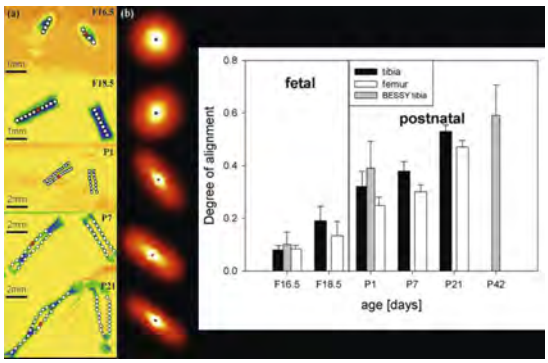

Fig. 3: (a) Radiography to define measuring positions of the SAXS measurements (b) representative two dimensional SAXS pattern of a single measurement point and (c) Rho-parameter, a measure of the degree of mineral particle alignment, analyzed dependent on age.

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Mechanobiology

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The structure of bone and its constituent material is constantly changing due to processes executed by different specialized cells. The stiffness of the bone material is changed by incorporation of mineral, the bone material is continuously remodeled and, after fracture, bone is able to heal. In these processes the behavior of cells is partly controlled by mechanical stimuli. How mechanical stimulation regulates in detail cell behavior is very challenging to study in animal experiments. Computer experiments, however, are an alternative approach to test our understanding of the mechanobiological control of processes in bone. In a computer model different hypotheses of cell reaction can be implemented, and the resulting consequences on the bone structure can then be compared with experiments.

Bone Healing

During bone healing a callus is temporarily formed around the fracture site for mechanical stabilization. Stem cells migrating to the fracture site are the biological basis for the formation of different tissues within this callus. The differentiation of the stem cells into specialized, tissue forming cells is partially mechanically controlled. In this way, low mechanical stimulation allows direct formation of bone, whereas strong stimulation results in cartilage formation. We studied the mechanobiological control of bone healing based on animal experiments on sheep with a histological documentation of the time course of the healing process performed at the Julius Wolff Institute at Charité, Berlin. The first challenge was to condense the available histological data in a succession of images that reflect the normal course of healing in sheep **[1]**. The inter-individual differences between sheep required the development of special image averaging tools to conserve the information of the temporal and spatial arrangement of different tissues in the fracture callus. Not only the arrangement of tissues evolve with time, but also the mechanical properties of the tissues themselves leading to a strong mechanical heterogeneity in the newly formed bone. The incorporation of recent experimental data in a Finite Element model allowed us to calculate the effect of this heterogeneity on the local strains within the callus **[2]**. With a phenomenological computer model of the healing process, we then investigated how the choice of the threshold values of the mechanical stimulus for bone and cartilage formation influence the course of healing (**Fig. 1**). It turned out that good agreement with the experimentally observed presence of cartilage in the callus is obtained only within a very restricted range of the threshold values and when assuming the outer skin of the broken bone to be the main source of the stem cells (**Fig. 2**) **[3]**.

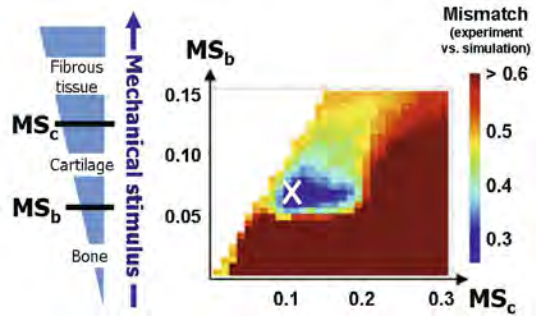

Fig. 1: Left, mechanical control of tissue formation during bone healing. Low stimulation leads to direct bone formation, whereas a higher stimulus results first in cartilage formation. Right, phase diagram summarizing a parameter study, where the threshold values of the mechanical stimulus for bone formation (MS_b) and cartilage formation (MS_c) were varied. Colors denote the agreement between experimental and simulational images with the white cross corresponding to the minimal mismatch.

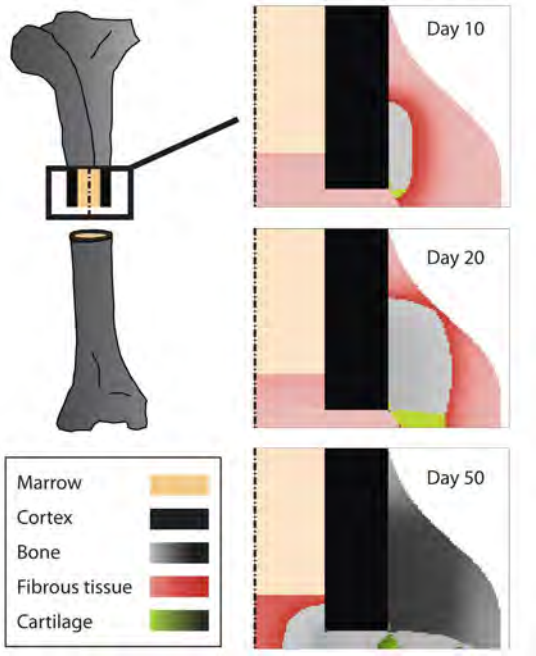

Fig. 2: The course of healing in good agreement with experimental observations obtained by a mechanobiological computer model. In the simulational images only the upper right part of the fracture with the broken cortex in black is shown. At intermediate stages of healing the bridging of the two cortex ends occurs via cartilage outside of the fracture gap.

Bone Remodeling and Structural Adaptation

The network-like architecture of trabecular bone is continuously remodeled by resorption and deposition of small bone packets from the bone surface. This remodeling process allows the trabecular structure to adapt itself to mechanical needs **[4]**. Striking evidence for the structural adaptation of

trabecular bone architecture can be found in the anisotropic arrangement of trabeculae in the proximal femur of humans and primates (**Fig. 3**). In cooperation with anthropologists, we made use of the natural variation of loading caused by a different main locomotor behavior of different primates and quantified the heterogeneity and anisotropy of the bone architecture **[5]**. Comparing the structure within the femoral head between a primate, which predominately walks, to one, which uses mainly the arms for locomotion, showed stronger anisotropy of the bone under higher load (**Fig. 3**).

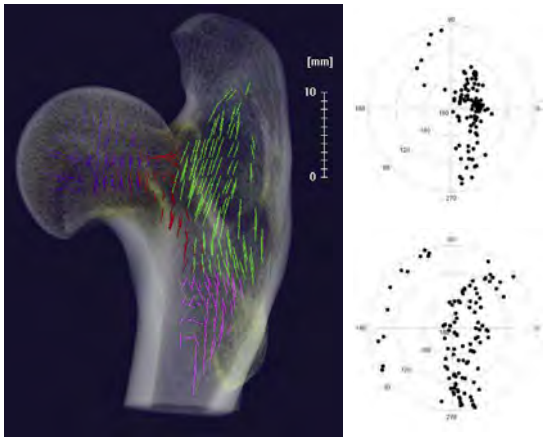

Fig. 3: Proximal femur of a baboon. The straight lines denote the local anisotropy of the trabecular bone architecture. Orientation of the lines represent the local main direction of the trabeculae, their lengths are proportional to the local degree of anisotropy. Different colors denote different anatomical regions: femoral head (blue), neck (red), shaft (pink) and greater trochanter (green). Right, the projection of the main local directions of the trabeculae onto a lower hemisphere, shows that the architecture for the "walking" baboon (top) is more anisotropic than the "brachiating" gibbon (bottom).

On the cellular level, structural adaptation to mechanical needs is realized via a mechanical control of the remodeling process. Osteocytes embedded within the bone matrix are thought to act as mechanical sensors, which signal to the bone surface the mechanical need for bone resorption or deposition. Using computer simulations we studied the influence of specific components in the mechanobiological system of cell interaction. First, different hypotheses were tested of how the mechanical stimulus for bone remodeling is integrated by osteocytes. A collective (summed) signal from multiple osteocytes as opposed to an individual (maximal) signal from a single osteocyte was found to lead to lower inner porosity and surface roughness of the simulated bone structure **[6]**. This observation can be interpreted that collective osteocyte signaling provides an effective surface tension to the remodeling process. Second, the relation between the mechanical signal reaching the cells at the bone surface and the probability for local bone resorption or deposition was studied. Simulations indicate that a threshold value for the mechanical stimulus has to be overcome to strongly activate deposition **[7]**.

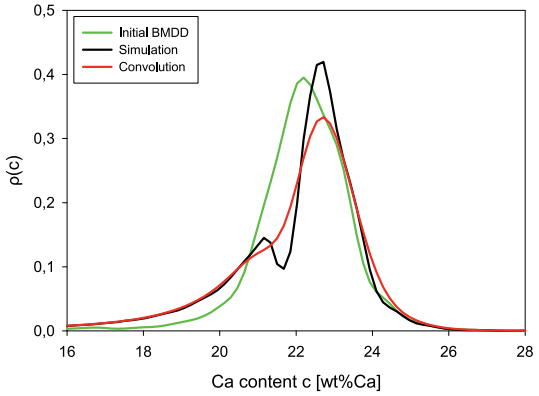

Fig. 4: Simulated time evolution of the bone mineralization density distribution (BMDD) after treatment with parathyroid hormone. The initial configuration (green) was obtained by deconvolving the measured BMDD before treatment. After 1.5 years the simulated BMDD (black) shows the formation of a second peak at about 21 wt% Ca. A measurement with a standard acquisition time of 100 seconds would show only a shoulder, but not a second peak (red).

Bone Mineralization

The continuous incorporation of mineral in a newly formed bone packet together with bone remodeling gives rise to a patchwork structure of bone packets with different mineral content. This material heterogeneity of bone can be quantified in a frequency distribution called the bone mineralization density distribution (BMDD). The BMDD has proven to be a sensitive diagnostic tool for bone diseases. Mathematical modeling allows connecting pathological changes in the BMDD with disturbances in bone remodeling and mineralization.

One limitation of the comparison between theoretical prediction and BMDD measurements is due to the fact that the experimental data are affected by the stochastic nature of the backscattering of electrons and the finite acquisition time. We have devised an approach using mathematical tools of regularization to deconvolve and correct measured BMDDs. As a result, the reference BMDD for healthy human adults could be defined with improved precision. This correction together with our computer model can further help to recover multiple peaks in the BMDD, which were smeared over by the measurement (**Fig. 4**). Our mathematical model was also applied to situations where the mineralization process is disturbed. This can occur, for example, by a tumor, which deranges mineral homeostasis by secreting hormones **[8]**. The inadequate mineralization in osteomalacia and the increased bone turnover at menopause both lead to a shift of the BMDD histogram towards lower mineral contents, in comparison to a healthy reference. With the use of mathematical modeling, it became possible to differentiate the time evolution of the BMDD, for both disease scenarios.

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Biochemical Strategies in Load-Bearing Natural Materials

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Biological organisms synthesize a diverse assortment of robust load-bearing materials from various combinations of simple organic biopolymers such as proteins or sugar chains and inorganic components such as ions or minerals. Additionally, biological materials have evolved to do this with a highly economical use of resources under environmentally friendly processing conditions. The resulting biologically produced materials often have interesting and technologically attractive properties that are not yet realized in engineering materials. For these reasons, it is of interest to understand the structure-function relationships that underlie the performance of biological materials.

Fig. 1: Mussels secure themselves to available surfaces with an array of fibers known as the byssus. Byssal threads are an attractive model system for biomimetic investigation because of their interesting mechanical properties, especially the ability to self-repair following load-induced damage.

In the new group "Biochemical strategies in load-bearing natural materials" (formed July 2010), we utilize a variety of methods including those in biochemistry, molecular biology, materials science, spectroscopy, and polymer science with the aim of establishing basic connections between the biochemical components of natural materials, their hierarchical organization and the resulting material properties. One model system that provides a unique opportunity for probing such questions is the byssus of marine mussels (**Fig. 1**). Mussels use the biopolymeric attachment fibers that make up the byssus to create a secure holdfast on surfaces in rocky seashore environments. The mechanical properties of byssal threads are specially tailored for their role as an abrasion resistant shock absorber and additionally, they exhibit impressive self-healing properties. Because they are composed almost entirely of protein, their material properties must arise from specific aspects of the protein building blocks.

Current research in the group is aimed at understanding the biochemical and structural factors that provide self-healing properties to byssal threads. Results indicate that coordination cross-links between metal ions and byssal proteins in the fibrous interior of threads may function as reversibly breakable bonds that rupture prior to the covalent bonds. In doing so, these sacrificial bonds dissipate mechanical energy and spare the whole structure from catastrophic failure. Apparently, these bonds reform once the load has been removed allowing threads to heal and recover initial material properties. These chemical concepts could potentially be applied to the production of self-healing polymeric fibers.

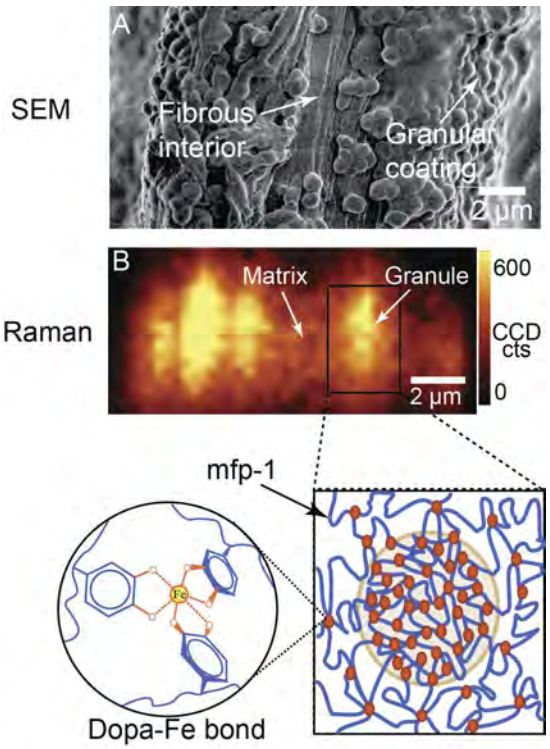

Fig. 2: (A) The outer cuticle of byssal threads is a thin and granular protective coating that uniquely combines hardness and extensibility. (B) Resonance Raman spectroscopy revealed that the cuticle consists of metallopolymeric protein (mfp-1) network with regions of high (granules) and low (matrix) dopa-Fe cross-link density. Granules thus provide cuticle hardness, whereas the matrix provides extensibility.

Prior to forming the new research group, I studied similar questions as an Alexander von Humboldt postdoctoral researcher. During this period, in collaboration with Admir Masic, I investigated the chemical composition of the outer cuticle of the byssal threads **[1]**. This thin protective coating serves to shield the fibers from abrasive damage by wave-borne debris and is interesting from a biomimetic perspective due to its remarkable combination of hardness and extensibility. *In situ* confocal Raman spectroscopic imaging revealed that the unique combination of properties arises from a non-homogenous distribution of metal coordination cross-links between iron ions and cuticle proteins (**Fig. 2**). Areas of high concentration (granules) are believed to provide the epoxy-like hardness of the material, whereas the areas of low concentration (matrix) provide the large extensibility and permit reversible crack-formation. This interaction was found to be mediated by an uncommon post-translationally modified amino acid known as 3,4-dihydroxyphenylalanine (dopa). Using Raman spectroscopy, similar dopa-Fe complexes were further identified in other regions of the thread including the attachment plaque, where they likely play a role in the adhesive properties of the byssus **[2]**.

In collaboration with researchers in the US, the biomimetically extracted chemical concepts from the byssus cuticle were adapted to synthesize metallopolymers that exhibited enhanced mechanical performance, including self-healing properties **[3]**. Specifically, dopa-Fe^{3+} crosslinks were integrated into a hydrogel network by employing a pH-dependent assembly process, mimicking the mussel thread formation process. At elevated pH, sticky gels were formed, which were able to recover initial material properties following mechanical failure. These studies provide support for the viability of such chemical level biomimetic approaches in designing and creating synthetic materials.

Additionally, in collaboration with the Plant Biomechanics group lead by Ingo Burgert, the actuation behavior of desert ice plants (Aizoaceae) was investigated in the framework of SPP-1420 program "Biomimetic Materials Research: Functionality by Hierarchical Structuring of Materials" **[4]**. The seed capsules of these plants are noteworthy because despite being non-living they undergo a complex and reversible actuated unfolding process during wetting and drying cycles (**Fig. 3A-B**). Our research found that seed capsules utilize a hierarchical arrangement of specialized swellable cells to orchestrate an Origami-like bi-directional movement in the whole structure (**Fig. 3C**). The extracted concepts from this actuated plant structure could have important implications for the growing field of "programmable matter".

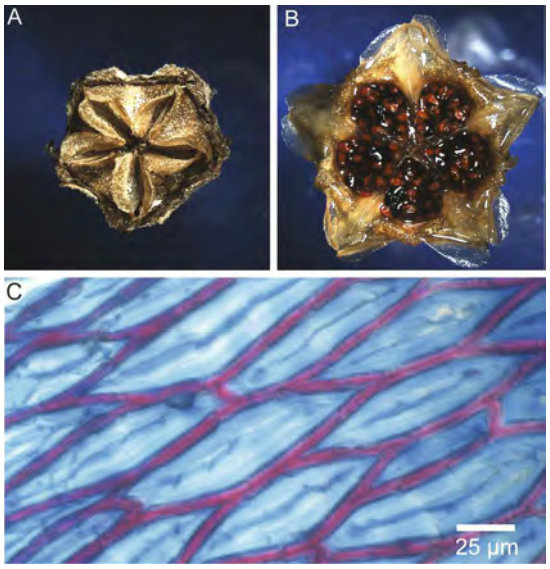

Fig. 3. (A-B) Seed capsules from the ice plant Delosperma nakurense have protective valves that unfold when hydrated. (C) Actuation of these non-living tissues is mediated by specialized cells containing a swellable cellulosic filler material.

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Spider Cuticle – A Study of the Structure-Function Relation

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The arthropods cuticle is a fascinating multifunctional material. It acts as a shield and a skeleton, but also comprises specialized tools and sensilla (sense organs). Its mechanical properties are thus finely tuned to stand the demands of its different functions. The main components of the cuticle are α-chitin (polyacetylglucosamine), arranged into crystalline fibrills (3nm wide, 300 nm long), and a protein matrix. The proteins adsorb on specific planes of the chitin crystals, forming higher order fibers. In spiders, these fibers form sheets which then stack in a plywood structure. The mechanical properties of the cuticle are determined by its composition, namely the chitin to protein ratio, cross-linking, and water content, and by structural factors, mainly fibers packing and orientation. Overall, these changes allow 20-fold variation in the cuticle stiffness.

Our study focuses on two extreme cuticle-based systems, each having very different mechanical demands: the vibration-sensing slit sensilla and the cheliceral-fangs used by spiders to inject prey with poison. We study the fiber arrangement at various size scales – from the molecular level to higher-order hierarchical organization – using X-ray scattering (SAXS) and diffraction (XRD) methods, electron microscopy and x-ray μCT. These findings are correlated with investigation of the mechanical properties with high spatial resolution techniques and in hydrated conditions, using scanning acoustic microscopy (SAM) and nano-indentation.

The Slit Sensilla and Lyriform Organ:
The strain sensitive slit sensilla are elongated openings in the cuticle. They are located on the legs, abdomen and chelicerae, and occur as single isolated slits or as a compound organ built of arrays of oriented slits (the lyriform organ). The slit sensilla react to minute deformations (in the order of a few Ångstoms (10-10m)) caused by internal (e.g. locomotion) or external (e.g. substrate vibration) sources, which make them one of the most sensitive sensory systems in the animal kingdom. The slit sensilla show also incredible specificity. The environmental signals are preferentially filtered such that only biologically-relevant signals are transferred to the nervous system, while other frequencies are filtered out. This allows interpretation of complex environmental signals with relatively little processing by the central nervous system. As such, the mechanosensors of spiders are a particularly interesting model for the design of materials with embedded sensory properties.

The Chelicerae
The cheliceral fangs of the wandering spider, Cupiennius salei, are curved hollow structures with a single opening of the venom canal close to the tip. The spider mostly feeds on insects, thus its fang has to puncture and cut through insect cuticle, made of similar material.The fiber orientation in the inner part of the fang is mainly parallel to its surface while in the outer part the fibers run concentrically. The outermost cuticular layer seems to contain no chitin fibers at all. In various invertebrates such as insects and worms reinforcement against wear is achieved by incorporation of transition metals e.g. Zn, Mn and Cu into the protein matrix. In others, Cu, Ca and Mg ions are deposited as various mineral forms. By means of x-ray fluorescence we have identified the presence of Zn, Mn Ca and Mg in the fangs. We also find correlation between the presence of the metal ions and increased mechanical properties of the cuticle, although the manner in which they are incorporated is still unknown. To address this question, we complement our structural study with a spectroscopic analysis, using IR and X-ray absorption spectroscopies (XANES and EXAFS).

A better understanding of the mechanisms evolved in these organisms to tailor the materials properties of the cuticle to fulfill different functions will also serve the design of sophisticated materials with desired mechanical properties and sensory functions.

The work is performed in a close collaboration of Prof. Friedrich Barth of the University of Vienna.

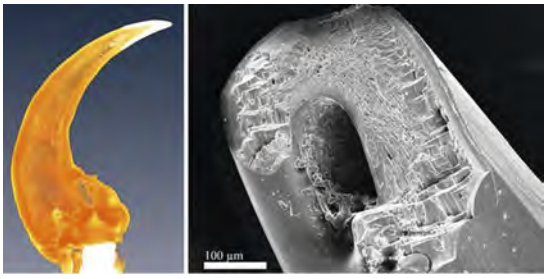

Fig. 1: The cheliceral fang of the wandering spider (a) a slice from a X-ray tomogram of the fang. The bright areas correspond to the higher density of the cuticle where the metals ions are incorporated. (b) Scanning electron micrograms of a fracture close to the tip of the chelicerae, at the opening of the venom canal.

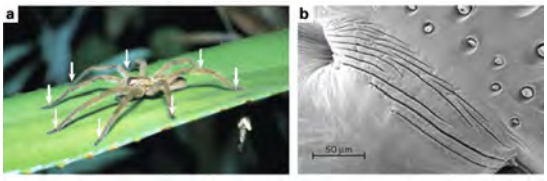

Fig. 2: Vibration-sensitive slit organ. a, Cupiennius salei, with arrows pointing to the location of the vibration sensors on the legs. B. Scanning electron micrograph of the vibration detector (dorsal view). Adapted from Ref. ***[3]***

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Calcified Cartilage in Shark Skeletons

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Calcified Cartilage in Shark Skeletons

The elasmobranch fishes (sharks, rays and relatives; **Fig. 1A**) are some of the fastest and largest animals in the ocean, and many can feed on extremely large or hard prey. This high performance is counterintuitive: the skeletons of these fishes are fashioned entirely of cartilage, which, unlike bone, is incapable of healing **[1-2]**. The morphology of this mineralized cartilage is strikingly different from that of mammals: most skeletal elements are sheathed in calcified tiles – "tesserae", each <500µm wide – covering the uncalcified cartilage underneath (**Fig. 1B,C**). This gross patterning of shark cartilage has been known for nearly two centuries, but the basic questions surrounding the material properties, micro/nanostructural organization and development of this tissue are barely addressed **[e.g. 2-4]**. A synthesis of my previous work and our current data suggests that important insight into mineralization processes can be gained by looking at chondrocytes (cartilage cells; **Fig. 1B,D**) in the mineralized and unmineralized tissues. As tessellation (tiling) is a vital feature of growth and mechanics in the skeleton **[2, 4]**, our work details the organization and functional advantages of the tissue.

The high functionality of elasmobranch cartilage is surely related to the unique arrangement of its mineralized tissue; the maintenance of the tiled pattern throughout life is therefore vital. To this end, as the skeleton grows, the number and/or size of tesserae must increase; the latter appears to be the predominant mechanism **[2]**. Tesserae grow by "engulfing" living chondrocytes from underlying uncalcified cartilage and entombing them in a highly cellular intratesseral network, interconnected by canalicular passageways analogous but considerably larger to those in bone **[5]** (**Fig. 1D,E**). Tissue samples from animals injected with a fluorescent marker for calcifying tissue (**Fig. 1F**) suggest that initial mineralization is localized around the cells themselves **[3]**. If the entombed cells are epicenters of skeletal growth and calcification (which continues throughout life); and, since deposited mineralized material cannot be removed in this tissue; the cells may be slowly "walling themselves in" by filling the space around them with permanent calcified tissue. Also, since tesserae increase in size as animals age, mineralizing material is surely distributed to and deposited at the tesseral margins. We therefore believe that the canalicular passages are critical to maintaining favorable cellular environments while aiding in distributing materials/products important to mineralization.

If these hypotheses of tissue growth are correct, these processes should be reflected in local variation in tissue properties and composition, with the degree of mineralization changing with distance from tesseral margins and from the cells themselves. Our current work supports this **[3]**: backscattered electron imaging (BEI) shows complex patterns of mineral variation in tesserae, concentric to cellular lacunae (spaces housing cells) and to tesseral edges, with tissue along the margins of tesserae and lacunae being less mineralized (**Fig. 1E**). Raman spectroscopic images of tesserae support the local variations in mineral content shown in BEI data and suggest an inverse correlation of mineral and collagen content; however these trends remain to be teased apart from effects resulting from variations in collagen fiber orientation (**Fig. 1G**). These data combined with x-ray scattering data, recently gathered at the local synchrotron facility (BESSY II), will describe the coordination and arrangement of organic and inorganic materials in tesserae. This will elucidate aspects of the framework around which the meta-pattern of skeletal "tiling" is based, perhaps providing clues to inform development of low-density, high-stiffness/high-damping engineering composites **[4]**. Our work also provides an important missing step in our understanding of skeletal tissue evolution, clarifying mineralization paradigms in the oldest surviving group of vertebrates with mineralized skeletons.

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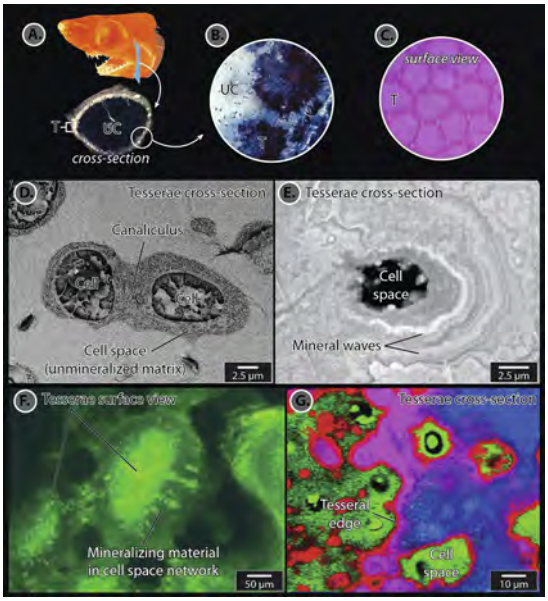

Fig. 1: The tessellated cartilage of sharks (A; lateral view of CT scan) is comprised of uncalcified cartilage, UC, overlain by a rind of calcified tiles (≤500µm wide) called tesserae, T, shown here in cross-sectional (B) and surface views (C). The cells inside tesserae (D, also visible in B) are living and connected to one another by short passageways – the waves of varying mineral density radiating out from cell spaces (E; BSE image), the movement of mineralizing tissue through the canalicular network (F; histology of oxytetracycline-injected animal), and the variation in chemical signature with distance from cells and tesseral margins (G; Raman hyperspectral image, colors represent distinct chemical spectra) provide clues cells' roles in growth mechanisms.

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Hierarchical Structure of Biological & Biomimetic Materials

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The role of structure in biological and biomimetic materials at different length scales is crucial for their mechanical properties and biological functions.

We investigate structural arrangements of cellular and organic constituents as well as mineral phases in biological tissues to learn more about formation, function and properties of these tissues. We use high-resolution two- and three-dimensional imaging techniques from material science to characterize the evolution of the micro- and nanostructure of various tissues. In bone tissues we aim to understand dynamic processes, such as mineralization of the organic matrix as it occurs during remodeling and bone healing. By applying *in situ* micromechanical and synchrotron-based methods on biological and biomimetic materials we elucidate basic mechanisms by which the structure controls the mechanical performance.

The Organization of the Osteocyte Network Mirrors the Extracellular Matrix Orientation in Bone

Bone is constantly undergoing remodeling as a result of the interplay between bone resorption by osteoclasts and bone formation by osteoblasts. During bone formation some of the osteoblasts are embedded in the mineralizing collagen matrix and differentiate to osteocytes, forming a network throughout the whole bone tissue.

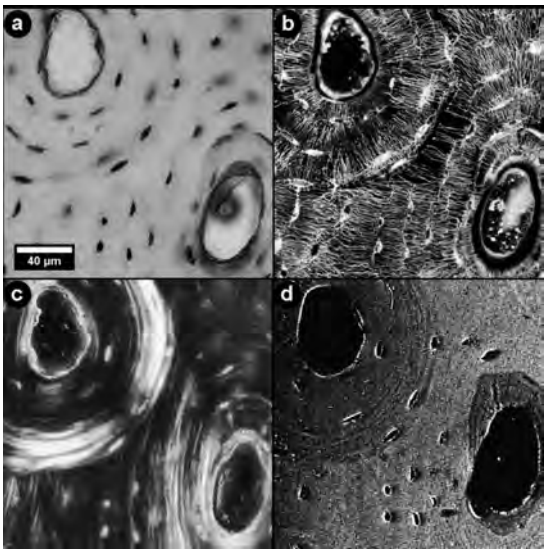

Fig. 1: Equine metacarpal bone: osteons, embedded in older bone matrix; (a) area visualized by light microscopy, (b) confocal microscopy, (c) polarized microscopy and (d) backscattered electron microscopy.

We investigated the extent to which the organization of the osteocyte network correlates with the collagen matrix arrangement in different bone tissues **[1]**. Several tissue types -with different degrees of organization- from equine, ovine and murine bone have been examined using three-dimensional imaging of osteocyte networks by confocal laser scanning microscopy. Furthermore, the tissues have been characterized by polarized light microscopy and back-scattered electron imaging (**Fig. 1**).

The spatial arrangement of unorganized and organized bone is shown schematically in **Fig. 2**. We conclude that osteoblasts synthesize and utilize scaffold-like tissue as a guide for the deposition of highly ordered and mechanically competent bone tissue by a collective action of many cells. The collective cell action is facilitated by a substrate layer whose surface directs this process. Without this substrate osteoblasts build microlamellar bone which is then used as a substrate layer.

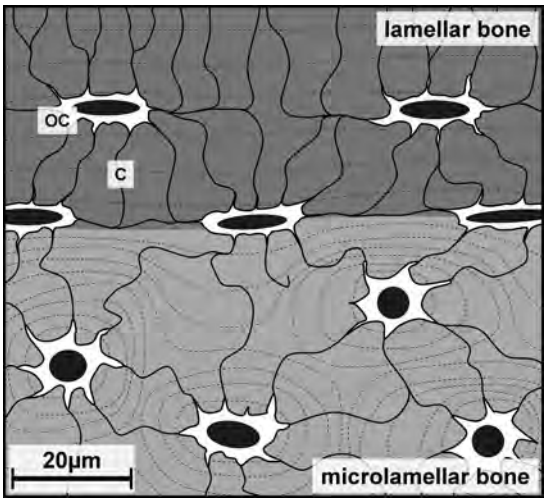

Fig. 2: Scheme of the osteocytic network and corresponding matrix orientation (red dashed lines). Top: lamellar bone layer with highly aligned osteocytic network; alignment of lacunae (OC) is parallel; canaliculi (C) run mainly perpendicular to the lamellae. Bottom: microlamellar bone with lower degree of organization; canaliculi run mainly radially from osteocytes.

Furthermore, we have qualitatively shown that primary bone in the callus of sheep bone has a low degree of order in cell organization and in collagen architecture **[2]**. Similar to formation of new bone, in fracture healing secondary lamellar bone is deposited on top of this scaffold-like primary structure.

In the context of bone tissue engineering, this encourages the idea that scaffolds mimicking the primary bone architecture may be developed to accelerate bone regeneration, for example in critical defect healing.

Microstructural Properties and Growth of Antler Bone

Bone appears in many forms, fulfilling numerous mechanical functions. One example of a particular tough bone material is deer antler. This is an exceptional biomineralized organ which is completely regenerated every year and is used as a fighting weapon by rival male deer.

We used time-resolved synchrotron small angle X-ray diffraction together with tensile testing of antler bone to elucidate the structural origin of the antler's high toughness **[3]**. It has been shown for other bone types **[4]** as well as synthetic materials, such as shape-memory polymers **[5]**, that *in situ* tensile testing in combination with X-ray diffraction is an appropriate tool to investigate deformation mechanisms simultaneously at different levels of hierarchy. The deformation at the nanoscale (fibril strain) could be determined from changes in the diffraction pattern during macroscopic tensile tests (tissue strain). The results show that in deer antler on average fibrils are strained only half as much as the whole tissue and the fibril strain increases linearly with tissue strain, both during elastic and inelastic deformation.

Fig. 3 shows the change in average strain (black circles) of the fibrils with increasing macroscopic tissue strain. The distance between upper and lower curves (white circles) is an indication of the width of the fibril strain distribution. During elastic deformation all curves rise linearly (same slope) with tissue strain implying all fibrils are stretched to the same extent. Most remarkably, beyond a certain tissue strain different fibrils start to show increasingly different degrees of elongation at the same macroscopic strain. This strain-inhomogeneity on the fibril level increases with tissue strain beyond the yield as indicated by the shaded region in **Fig. 3**. The average fibril strain rises linearly until sample failure. This inhomogeneous fibrillar strain pattern at the nanoscale may explain the extreme toughness of antler compared to normal bone.

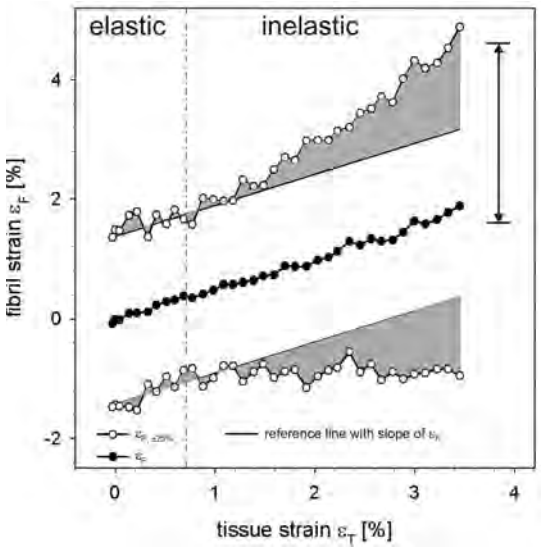

Figure 3: Average fibril strain ε_F (black circles) in antler bone plotted against tissue strain ε_T as determined from in situ x-ray tensile tests. Upper and lower limits of the fibril strain distribution $\varepsilon_{F,\pm 25\%}$ within the X-ray scattering volume are plotted as white circles. The average fibril strain ε_F increases linearly in both the elastic and inelastic range. The bidirectional arrow on the right displays the mean fibril strain range at 100% mean macroscopic fracture strain.

Further studies on antler, looking at the extremely fast growth from a material-design-perspective, show that antler bone growth takes place via at least two scaffold structures, the mineralized cartilage and the bone framework respectively. These scaffolds are characterized by a highly anisotropic tubular architecture. Maturation of antler cortical tissue occurs by directed bone ingrowth into the bone framework: a highly mineralized, lamellar bone matrix with varying fiber orientations is filled by less mineralized, longitudinally oriented bone rods (primary osteons).

This material design, containing interfaces between structural features with different properties, may also lead to an increase in toughness and prevent crack initiation and propagation.

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Plant Biomechanics and Biomimetics

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2007: Habilitation in Plant Biology (Humboldt University, Berlin) Thesis: On the mechanical design of plant cell walls

The Plant Biomechanics and Biomimetics research group is interested in the structure-function-relationships of plants mainly at the micro-and nanoscale. We intend to understand the underlying principles of how plants accomplish their excellent mechanical performance and how tissues are pre-stressed during growth. The gained knowledge allows for a deeper insight into plant strategies to mechanically adapt to environmental conditions as well as the mechanisms of plant movements, for instance for effective seed dispersal. The examined biological systems are valuable sources for extracting biomimetic principles as the specific functionality is achieved by a clever structuring which turns even dead plant tissues into active and responsive devices.

The group research profile comprises three main activities; the analyses of structure and properties of plant cell walls, the generation of stresses and plant movements as well as projects towards a biomimetic transfer of the unravelled principles. The methods utilized are tensile tests to investigate tissue and fibre mechanical properties in combination with (nano)structural examination techniques such as X-ray scattering, Raman spectroscopy, Environmental Scanning Electron microscopy and cryo-SEM.

Cell Wall Structure and Properties

The plant cell wall represents a fibre-reinforced polymer assembly of stiff cellulose fibrils of a few nanometers in diameter, embedded in soft matrix macromolecules (hemicelluloses, pectins, lignin, structural proteins). The mechanical design of this nano-composite is analyzed, in order to gain better insights into optimization strategies of living plants as well as into the material design of cell walls **[1]**. These investigations are conducted on thin and flexible primary cell walls which allow the living cell to grow and on thick and rigid lignified secondary cell walls which mechanically stabilize the plant body. Both cell wall systems are investigated in both the natural condition as well as in a genetically modified state. This is done in close collaboration with colleagues from the fields of plant physiology, biochemistry and molecular biology. Collaboration exists on campus with the MPI for Molecular Plant Physiology (MPI-MP), Potsdam as well as with partners from the recently expired EU-Project CASPIC.

In terms of primary cell walls mechanical analysis was performed on Arabidopsis hypocotyls of various transgene lines and chemical pre-treatments, each affecting one of the crucial cell wall components. Plants with modification in xyloglucan structure were investigated together with the Markus Pauly Lab (Berkeley). In collaboration with Herman Höfte (INRA-Versailles) we studied modified Arabidopsis plants with alterations in the protein structure of the cellulose synthase complexes and the pectin composition **[2]**. The mechanical performance of Arabidopsis plants with alterations in the cytoskeleton and/or in the cellulose synthase complexes was investigated together with Staffan Persson from the MPI-MP.

In terms of secondary cell walls most research activities were based on transgene aspen plants which were examined in collaboration with the lab of Björn Sundberg, Plant Science Center, Umea, Sweden. Here we investigated how the genetic modification affected cell wall nanostructure and mechanical performance. Besides micro-mechanical tests, the cellulose fibril orientation and cellulose fibril/ matrix interactions were investigated by X-ray scattering and Raman microscopy. Studies on a mutant with a lignin content reduced by ~30% showed only minor differences in tensile properties compared to the wildtype **[3]**.

In de- and rehydration experiments, combined with simultaneous X-ray diffraction measurements and tensile straining, we investigated together with Peter Fratzl how moisture changes below the fibre saturation point affect the crystal lattice of the cellulose fibrils in the wood cell wall (**Fig. 1**).

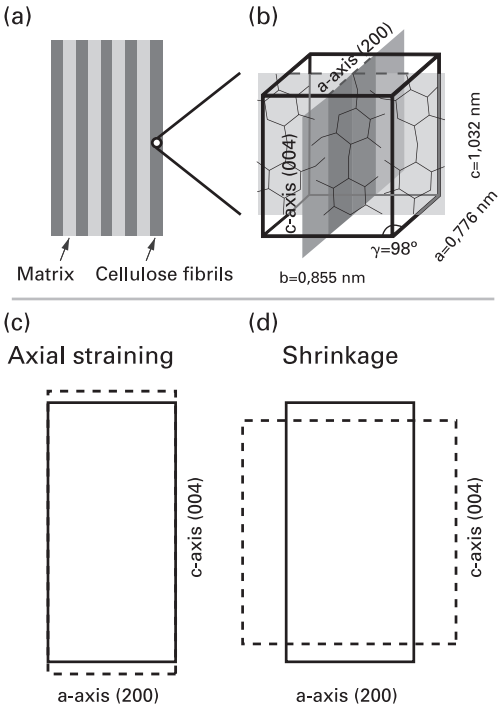

*Fig. 1: Schematic of (a) the alternating cellulose fibril – matrix structure in the cell wall and (b) of the axis of the crystal structure of cellulose. Deformation of the crystal lattice of cellulose due to (c) axial tensile loading and (d) drying **[4]**.*

Axial stresses resulted in a longitudinal expansion without significant changes in the transverse direction whereas during drying a longitudinal contraction and transverse expansion of the crystalline cellulose was measured. In view of the high stiffness of crystalline cellulose, the magnitude of the deformation can not be explained by stresses generated by the shrinking matrix molecules. It is more likely that water adsorption and desorption at the cellulose surface accounts for the moisture dependent changes in the dimensions of the cellulose crystal lattice **[4]**.

Further studies on structure-function-relationships in plants were aiming at understanding the basic principles of the organization of stiffness gradients between tissues. Here we studied the gradient transitions in structure and mechanical properties of individual wood cells across a growth ring of spruce **[5]** and the design of structural and mechanical interfaces between tissues in the giant reed (*Arundo donax*) **[6]**.

Stress Generation and Plant Movement

Research on the mechanisms of stress generation and plant movement is conducted in close cooperation with Peter Fratzl **[7]**.

After having studied stress generation in tension wood of hardwoods, we examined in a recent study the root contraction in perennial plants. Also for the roots of red clover we found tension wood fibres with the characteristic gelatinous layer (G-layer) filling the lumen of the cells. Raman microscopy studies and measurements of tissue deformation after enzymatic removal of the G-layer suggested that the mechanism of root contraction is similar to stress generation in tension wood of poplar **[8]** (**Fig. 2**).

However, tension wood of trees is optimized for generating high stresses and small deformation whereas contractile roots need to be largely deformed with little stresses involved. Investigations on how the system is structurally fine-tuned to be able to fulfill both opposed functions are ongoing.

In the framework of the SPP 1420 we run a project on the unfolding mechanism of ice plant seed capsules in collaboration with Christoph Neinhuis (TU-Dresden). These capsules show a complex opening mechanism upon wetting for seed dispersal. Interestingly also in this plant a gelatinous layer was found. Here, the highly swellable layer forces the cells to deform almost exclusively in one of the transverse directions which enables such large deformations of the valves upon wetting (see also report by Matt Harrington).

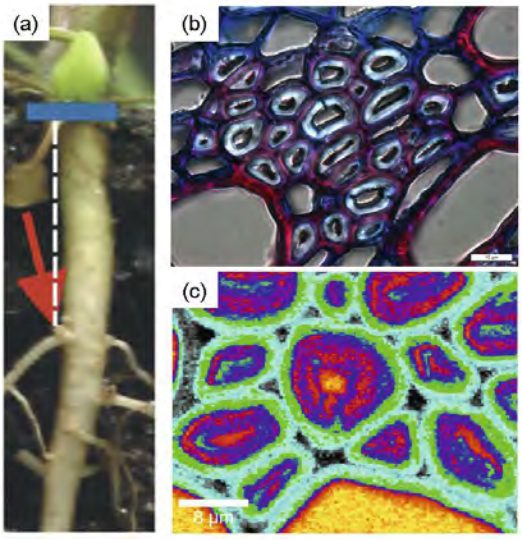

*Fig. 2: (a) Contractile root of red clover at an age of 13 weeks (b) cross-section with tension fibres containing the blue-stained G-layer in the lumen, (c) Raman microscopy image of water content showing that the G-layer in the lumen (red colour) contains more water than the surrounding cell wall layers (green colour) **[8]**.*

Bio-Inspired Materials

In two projects in collaboration with partners from the Departments of Colloid Chemistry and Interfaces as well as the universities of Freiburg and Bayreuth and the ITV-Denkendorf we are aiming at transferring the design principles of plant cell walls to synthetic systems. In the first project we have produced anisotropic Agarose hydrogels by embedding cellulose nanowhiskers and orienting them through external tensile straining. In the second project we intend to develop innovative glass fibre composites in the framework of a BMBF project. Here the group of Helmut Schlaad has developed a synthesis strategy which allows binding polymer chains of various lengths to the glass fibre surface. In single fibre pull out tests, conducted in our lab, we investigate whether the toughness of the fibre-reinforced composite can be increased by this approach. Further a review article about bio-inspired materials research has been published **[9]**.

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Biomimetic Actuation and Tissue Growth

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Compared to an Engineer, who can access the entire periodic table, Nature uses only a limited palette of elements to make structural materials. Despite this, a wide range of material properties is achieved by combining these elements into a composite material **[1, 2]**. Many of these natural materials are fibrous composites, in which the material properties are controlled precisely by the architectural arrangement of the fibres. On one hand it is important to understand the role of architecture on the resultant material properties and on the other hand how a particular tissue architecture is achieved during growth. These two themes are investigated in this group through three different topics: 1) by understanding the link between hygroscopic actuation in plant organs and the underlying tissue architecture (with I. Burgert, Plant Biomechanics Group, R. Elbaum and Y. Abraham, Hebrew Uni. Jerusalem, Y. Bréchet, INP-Grenoble and T Antretter, Uni. Leoben), 2) through the analysis of tissue orientation in the early stages of bone fracture healing (with A. Masic, Biomaterials Department and G. Duda at the Charité-Berlin); and 3) by studying how substrate geometry controls tissue growth (with, M. Rumpler, Boltzmann Institute, Vienna, F. D. Fischer, and E. Gamsjäger Uni. Leoben). The three themes share a common thread in that they deal with understanding the mechanics of shape and volume changes in fibrous tissues.

Controlling Actuation Through Architecture

Many plants have organs that can move in complex ways, controlled by a clever organisation of their underlying tissues. Examples include the awns of wheat or the stalksbill which are used to help propel seeds along and into the ground, and the opening of the scales on pine-cones or the valves on the ice-plant to allow for seed release (see I. Burgert and M. Harrington – Plant Biomechanics). In all of these systems actuation occurs in dead tissue which swells/contracts in controlled ways due to changes in external humidity. As these systems require no active energy transport by the plant, it is therefore the architecture of the tissue which gives rise to the complex movements. Our goal therefore is to understand the link between the architecture arrangement of swellable tissues and the resultant motion. A simple example of the effect of architecture on movement is given in **Fig. 1**. Here simple composite beams with a uniform cross-section have been simulated. The beam consists of two materials, active and swellable (grey) and passive and non-swellable (white), distributed uniformly along the beam, however with different symmetric arrangements within the cross sections (top row). Results of finite element simulations (bottom row) demonstrate that the symmetry of motion is controlled by the symmetry of the tissue architecture. Even if the materials are arranged only in two dimensions a large variety of three dimensional responses can still be achieved.

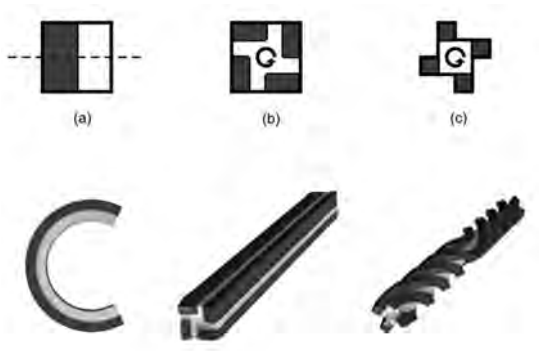

*Fig. 1: Three examples of how different arrangements of active (grey) and passive (white) materials over a cross section of a beam can influence the resultant actuation behaviour, leading to a) bending, to b) no macroscopic response, to c) twisting **[3]**.*

Collagen Organisation in Fracture Healing

The healing of fractured bone is a complex process in which an organised architecture of mineralised collagen fibrils is formed within the fracture gap. Recent work (Y. Liu Dept. Biomaterials) suggests that the formation of mineralised tissue during bone healing occurs in two "waves", an initial wave in which a scaffold of unorganised bone is quickly formed upon which a second wave of more organised lamellar bone is then produced. One issue that is still not understood is how the first scaffold of woven bone is produced and organised during the initial phases of healing when the tissue is not yet mineralised. We together with A. Masic (Biomaterials) and G. Duda (Charité) are currently investigating this in fracture calluses of rats, using the powerful technique of polarised Raman microspectroscopic imaging **[4]**. This technique allows us to produce maps of the spatial distribution and orientation of particular chemical groups such as collagen and mineral (**Fig. 2**). The initial data suggests that even in the early stages of healing the tissue becomes highly oriented, leading to an organised structure which is then the scaffold for the "second wave".

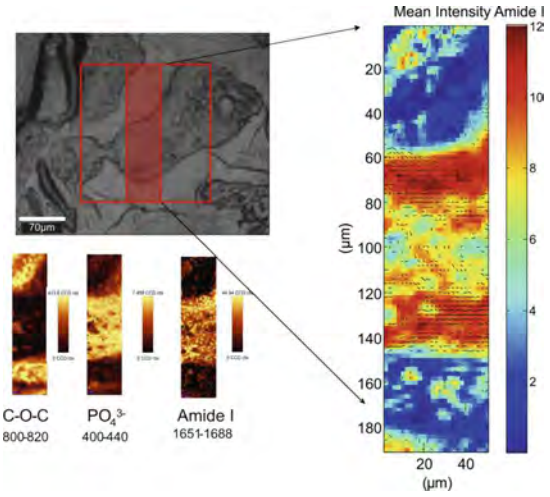

Fig. 2: Polarised raman imaging of mineralised cartilage in the rat fracture callus. The top left image is an optical micrograph of the region studied. The bottom images show chemical maps (unpolarised) of embedding material, mineral and collagen respectively. The black lines in the image on the right show the collagen orientation in the cartilage.

Geometric Control of Tissue Growth

An important focus of the group is towards gaining a more fundamental understanding of how growing tissues organise themselves inside a scaffold. By using rapid-prototyping to produce scaffolds of controlled shapes and sizes, we have shown that the tissue growth rate inside a pore correlates with the local curvature of the substrate **[5]**. This curvature controlled growth is similar to phase transformations in physics where surface tension plays an important role. In addition, it was also demonstrated that this rate of growth becomes independent of the material properties of the underlying substrate after the first cell layers were formed **[6]**, highlighting the importance of geometry on growth. In order to understand this more deeply we combine cell culture experiments with numerical simulations at different levels of complexity.

A hint towards understanding the mechanisms underlying geometric controlled tissue growth is found in the organisation of the actin cytoskeleton in tissue grown inside circular and square pores (**Fig. 3**). The actin stress filaments are aligned with the tissue border and are more concentrated close to the tissue surface, highlighting the role mechanical stresses play on growth. With this in mind we have developed a continuum model for tissue growth in confined geometries (with F. D. Fischer and E. Gamsjäger, Univ. Leoben) **[7]**. In this model a growth law consistent with the second law of thermodynamics was derived using Onsager's principle of maximum dissipation and applied to simple pore geometries. The model reproduces the observed dependence of the growth kinetics on the sign of curvature only when an explicit surface stress is introduced.

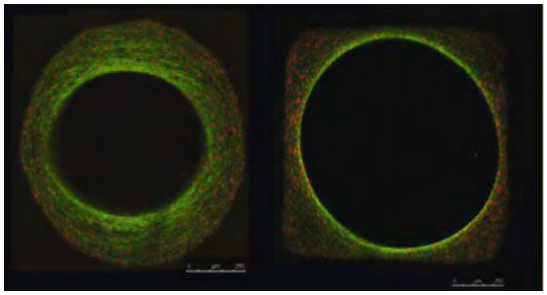

Figure 3: Confocal microscopy images of the actin cytoskeleton (green) and nuclei (red) after tissue growth by mouse pre-osteoblast cells (MC3T3-E1). Note the organisation of the actin filaments and the preferential tissue growth in the pore corners.

The fundamental understanding of the mechanisms of tissue growth has important implications in bone remodelling **[8]**, bone healing as well as in scaffold design for tissue engineering. This is highlighted in **Fig. 4** which shows the measured growth kinetics in square and cross shaped pores. By simply changing the pore geometry it was possible to accelerate tissue growth by a factor two without the addition of any other growth factors. The concept that local curvature determines growth was implemented into a numerical simulation based on actual images of the scaffolds to predict the time course of the projected tissue area. Although the growth behaviour is described well for early growth stages, by this curvature driven growth model (**Fig. 4**), further work is required to characterise and model the response of individual cells to their mechanical/geometrical environment.

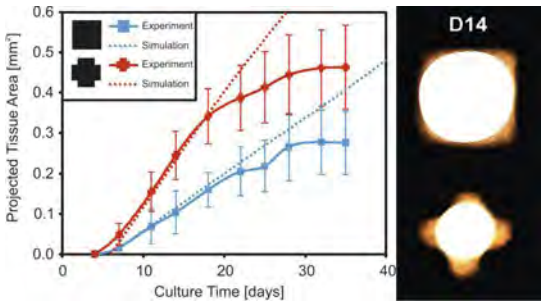

Figure 4: Tissue growth kinetics (left) measured in different shaped pores (right) compared to a simple curvature driven growth model (dotted lines).

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Magnetite and Hierarchical Systems

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Nature not only provides inspiration for designing new materials but also teaches us how to use interparticle and external forces to structure and assemble these building blocks into functional entities. Magnetotactic bacteria (**Fig. 1**) and their chain of magnetosomes represent a striking example of such an accomplishment where a simple living organism precisely tunes the properties of inorganics that in turn guide the cell movement thereby providing an energetic advantage vs. the non-magnetotactic counterparts **[1]**.
In my group, we have developed a bio-inspired research based on magnetotactic bacteria. This research combines the recent developments of nanoscale engineering in the chemical science and the latest advances in molecular biology. Thereby we have created a novel methodology enabling first, the understanding of the control of biological determinants over single inorganic building blocks at the nanoscale and over highly-organized hierarchical structures, and second, the use of these biomacromolecules to construct new functional materials.

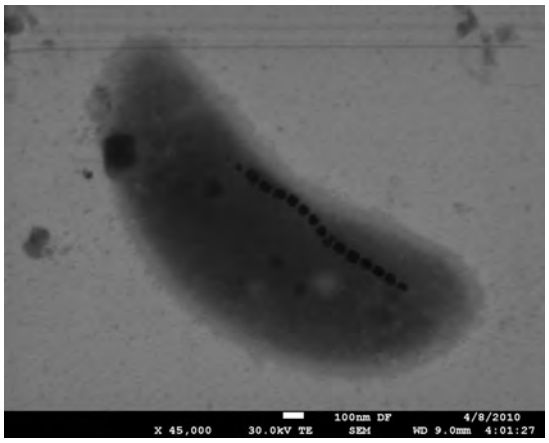

Fig. 1: a typical STEM image from a magnetotactic bacterium (strain AMB-1). The magnetosomes are the electron-dense particles that are aligned and form chain in the cells.

Biological Materials

Magnetosomes: Hierarchy at the Structural Level

The biomineralization of magnetite inside the magnetosome organelle together with the chain formation in magnetotactic bacteria are two processes that are highly controlled at the cellular level in order to form cellular magnetic dipoles. The smallest building block of this assembly is the magnetosome crystal. However, only controversial results about its microstructure were obtained so far, and the influence of the ultrastructure in the formation of the magnetic dipole i.e. on the function of the assembly is to be specified. We have thus investigated the structure of the magnetosomes using high-resolution synchrotron X-ray diffraction at the microspot beamline of the BESSY II synchrotron of the Helmholtz Zentrum Berlin **[2]**. Significant differences in lattice parameter were identified between intracellular magnetosomes from cultured magnetotactic bacteria and isolated ones (**Fig. 2**). Through comparison with abiotic control materials of similar size, we showed that this difference could be associated to different oxidation states and that the biogenic nanomagnetite was stoichiometric, i.e. structurally pure, whereas isolated magnetosomes were slightly oxidized. The hierarchical structuring of the magnetosome chain thus starts with the formation of structurally pure magnetite nanoparticles that in turn might influence the magnetic property of the magnetosome chains.

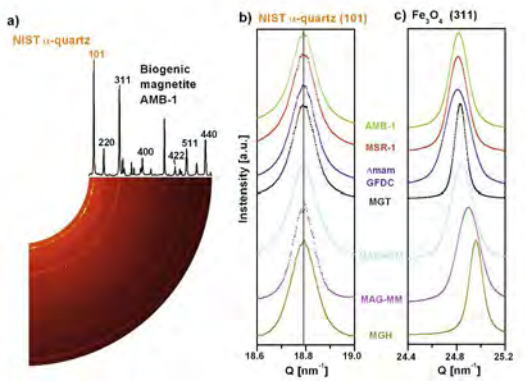

*Fig. 2: **a)** Exemplary 90° sector of AMB-1 diffraction pattern to visualize the azimuthal integration. Analyzed magnetite peaks and calibration peak (NIST α-quartz) indexed **b)** α-quartz (101) calibration peaks of different biogenic and abiotic magnetite/ maghemite samples. All peaks calibrated to Q = 18.7910nm^{-1} **c)** most intensive (311) reflex of all analyzed samples. Remarkable peak shift bet-ween biogenic magnetite in cell solution samples (AMB-1, MSR-1 and ΔmamGFDC) compared to isolated magnetosomal magnetite with and without membrane (MAG+MM and MAG-MM) and inorganic magnetite (MGT) or even more pronounced with maghemite (MGH).*

Magnetosomes Chains: Hierarchy at the Chain Level

Magnetotactic bacteria benefit from their ability to form cellular magnetic dipoles by assembling stable single-domain ferromagnetic particles in chains as a means to navigate along Earth's magnetic field lines on their way to favourable habitats. After studying the smallest building-blocks, i.e. the magnetosomes and their ultrastructure, we studied their assembly with FORC diagrams and ferromagnetic resonance

spectroscopy in order to again find how the chain can function as an entity **[3, 4]**. Magnetospirillum gryphiswaldense was cultured in a time-resolved experimental setting. Our data showed first that magnetic particle growth was not synchronized. Moreover, we could also show that the increase in particle numbers was insufficient to build up cellular magnetic dipoles. Finally dipoles of assembled magnetosome blocks occurred when the first magnetite particles reached a stable single-domain state. These stable single-domain particles could act as magnetic docks to stabilize the remaining and/or newly nucleated superparamagnetic particles in their adjacencies (**Fig. 3**). We thus could postulate that docking was a key mechanism for the building of the functional cellular magnetic dipole, which in turn controls the cells orientation.

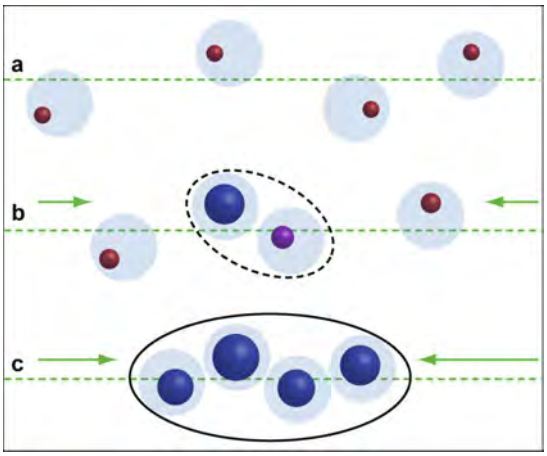

Fig. 3: Schematic sequence of cellular magnetic dipole formation. Superparamagnetic (SPM) magnetite particles (red) are nucleated in widely-spaced organelles (light blue), the green arrows indicate the biologically-driven movements of the magnetosomes along the cytoskeletal filament (dashed line) (a), stable single domain magnetite (blue dot) and its magnetic interaction (dashed-lined ellipse) act as "magnetic dock" to stabilize SPM particle (purple dot) (b). Spacing and size of magnetite are optimized, and the closed-neighbored magnetite particles separated only by magnetosome membrane generate a robust cellular magnetic dipole (solid-lined ellipse) (c). (from Faivre et al. (2010))

Biomimetic Materials

Synthetic Magnetite Nanoparticles: Studying the Initial Stages of Mineral Formation

Multiple synthetic routes for the production of magnetite nanoparticles have been reported in the literature. Indeed, the ferrimagnetic properties of such particles are increasingly exploited in bio- and nanotechnological applications. However, the formation mechanism has remained unclear. Crystallization pathways involving precipitation from soluble iron species or solid state transformations have been proposed. We have developed a set-up for the controlled formation of magnetite *in vitro* (**Fig. 4**) **[5]**. We are currently using high-resolution cryo-transmission electron microscopy to unravel the mechanism of such a formation. Our initial results indicate that magnetite forms from gradually transforming iron oxyhydroxide precursor clusters. These clusters build up colloidal crystalline assemblies, which fuse and become single or polycrystalline magnetite nanoparticles. These results are an essential step forward in the understanding of crystal formation in synthetic, geological and biomineralizing systems and will enable us to proceed to the next step of magnetite formation in the presence of biological determinant, i.e. additives found in magnetotactic bacteria.

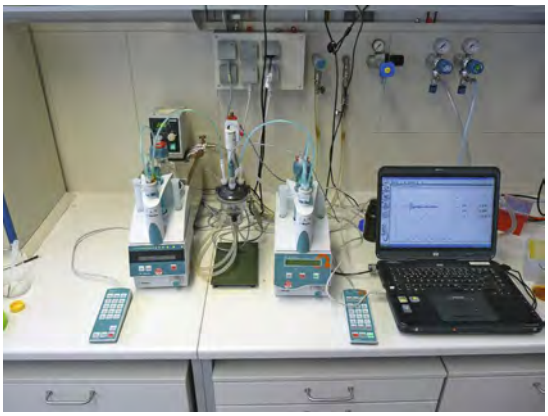

Fig. 4: set-up for the biomimetic syntheses.

Biomimetic Chains: Hierarchy in a Synthetic System

Hierarchical structuring of single particles can lead to the formation of multifunctional materials **[6]**. We are thus are interested in the biomimetic arrangement of the magnetic particles we form *in vitro* in a project funded within the 1420 Priority Programme of the DFG. 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, over-expression and isolation of MamK are currently underway to aid physical patterning of the biomimetic nanoparticles.

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Bio-Inspired Hybrid Materials and Synchrotron Research

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Biominerals are our source of inspiration for the design of new hybrid materials. Showing a great diversity in their structure and composition, biominerals can fulfill many different functions, ranging from load bearing and wear resistance to magnetic and optical sensing. Important concepts found in biominerals used for mechanical purposes are a large amount of organic-inorganic interfaces and structural hierarchy **[1]**. The formation of biominerals is to a large degree controlled by organic molecules. In this context, we studied the self-assembly of amelogenin proteins and their role in the biomineralization of tooth enamel. We found evidence for an oblate shape of amelogenin nanoparticles in suspension. The anisometric shape helps to explain the formation of previously observed anisotropic higher order structures which are believed to play a critical role in regulating the parallel arrangement of the hydroxyapatite crystals in enamel **[2]**. In addition to the formation of biominerals, we investigate their structure, stability and mechanical properties. Examples from crayfish and a mollusk shell are given in the following paragraphs. Our research is mainly focused on the lower hierarchical levels, i.e. the nanostructure and lattice structure. The most important questions that we address are which mechanisms contribute to stabilize amorphous biominerals and how organic molecules can get incorporated into mineral crystals. Comparative studies on bio-inspired model systems allow for deriving general concepts which can in the future help to develop new materials for technical applications. Our main experimental methods are synchrotron small- and wide- angle X-ray scattering (SAXS and WAXS), in particular at the MPI's experimental stage (μ-Spot beamline) of the BESSY II storage ring (Helmholtz-Zentrum Berlin).

Calcium Carbonate and Phosphate in Crayfish

In cooperation with scientists from the Ben-Gurion University in Israel we investigate the biomineralization of the freshwater crayfish *Cherax quadricarinatus*. The cuticle of this crustacean, which is regularly shed during every molting cycle, is reinforced with amorphous calcium carbonate. Surprisingly, investigations of the mandible of *C. quadricarinatus* showed that the molar extension, which is used for grinding, does not only consist of chitin and amorphous mineral, but also has a coating of crystalline apatite (see **Fig. 1**). This occurrence of apatite is very unusual for a crustacean. The structure and orientation of the apatite crystals found in the crayfish tooth are reminiscent of mammalian enamel. Moreover, the hardness profile of the crayfish molar, as measured by means of nanoindentation, was found to be remarkably similar to that of human teeth. Hence, the crayfish molar serves as an interesting example for the convergent evolution of a functional structure comparable to mammalian teeth. Furthermore, the crayfish mandibles as well as the crayfish gastroliths, which serve as calcium storage organs prior to molting, are used to study the effects of phosphate and different proteins for stabilizing amorphous calcium carbonate.

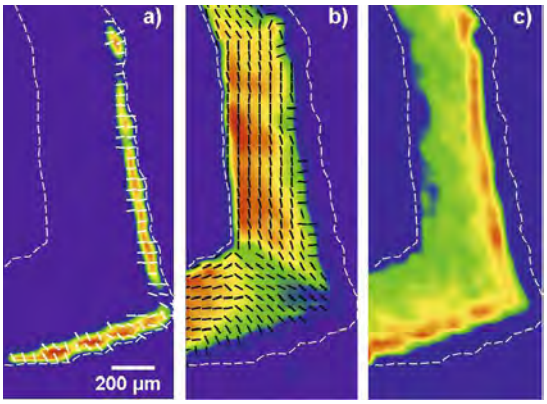

Fig. 1: Distribution of apatite (a), chitin (b) and amorphous mineral (c) in the molar of the crayfish Cherax quadricarinatus, evaluated from scanning WAXS measurements. The white and black lines in (a) and (b) indicate the orientation of the crystallographic c-axes of apatite and chitin, respectively. The dashed line follows the contour of the tooth cross section.

Biogenic Calcite Prisms from Mollusk Shells

Calcite from the outer layer of mollusk shells is known to contain intra-crystalline organic inclusions. We studied isolated calcite prisms from the shell of *Pinna nobilis* by means of combined synchrotron SAXS and WAXS **[3]**. A 3-dimensional reconstruction of the scattered intensity enabled us to relate the orientation of the nanostructure (SAXS signal arising from organic inclusions) to the crystallographic directions of the calcite lattice (WAXS). The results are shown as a stereographic projection of the integrated SAXS intensity (grey scale) together with the wide-angle spots of different calcite lattice planes as indicated by arrows (**Fig. 2**). A comparison of native and annealed calcite prisms, where the contrast for the latter is enhanced due to the removal of organics, shows that the organic-inorganic interfaces are preferentially oriented along the highly charged (001) lattice planes, most likely due to a strong interaction with negatively charged aspartate groups of the intra-crystalline proteins **[3]**.

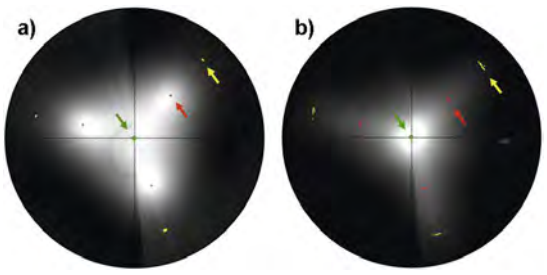

Fig. 2: Stereographic projection of SAXS intensity (grey scale) and wide-angle diffraction spots (green=(001), red=(104), yellow=(202)) for a native (a) and annealed (b) calcite prism isolated from a Pinna nobilis mollusk shell.

The observed (001) type interfaces help to explain the origin of previously reported lattice distortions in biogenic calcite, where the maximum distortion was found along the calcite c-axis. Moreover, additional studies on powder samples of prisms annealed at different temperatures gave proof that an initially rough organic-inorganic surface smoothens at 250° C **[3]**. This transition temperature coincides exactly with the one for the relaxation of the lattice parameters.

Bio-Inspired Calcite-Polyelectrolyte Particles

In order to find out whether we can observe similar effects as for the biogenic calcite, we investigate bio-inspired calcite particles with inclusions of polystyrenesulfonate (PSS). The work is carried out in cooperation with the Department of Colloid Chemistry. In spite of using only one soluble additive, we observed a highly complex hierarchical structure **[4]** (see **Fig. 3**).

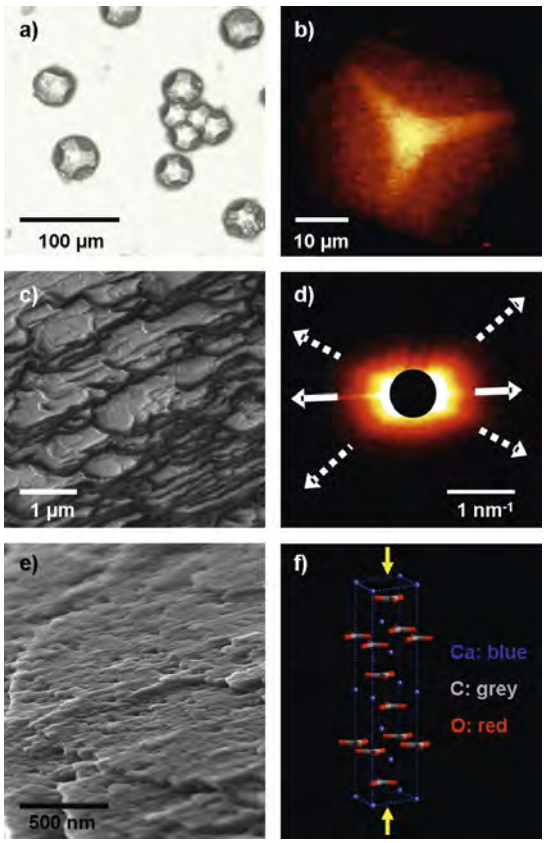

Fig. 3: Hierarchical structure of bio-inspired calcite-PSS hybrid particles: a) Light micrograph, b) Raman imaging of PSS (sulfonate group), c) SEM showing mineral building blocks, d) SAXS signal from interfaces with preferred orientations (dashed arrows: (104), full arrows: (001)), e) high resolution SEM showing a granular substructure, f) unit cell of the slightly distorted calcite lattice. The direction of the maximum contraction (c-axis) is indicated by yellow arrows.

The calcite-PSS hybrid particles, which are nucleated on the (001) plane, exhibit rounded edges (a) and variations in the polymer/mineral ratio on the µm-level (b). The intra-crystalline polyelectrolyte molecules induce a meso-scale arrangement of mineral building blocks in the 100 nm range (c), which show preferred orientations (d). Similar to biogenic calcite, the occurrence of organic-inorganic (001) interfaces in addition to the low energy (104) planes, arises from the interaction with negatively charged groups of the organic inclusions (aspartate in biogenic and sulfonate in biomimetic calcite). In addition, we observed a granular substructure of the mineral units (e) as well as a distortion of the calcite lattice structure (f), which is, however, much smaller than the effects previously found in biogenic calcite. The maximum distortion of the bio-inspired calcite, measured by means of high resolution X-ray diffraction at the European Synchrotron Radiation Facility in France, was a contraction of only 0.02% along the direction of the c-axes **[4]**.

Synchrotron Research at the µ-Spot Beamline

Together with different research groups of the MPI of Colloids and Interfaces, a wide range of materials including biological samples of bone, teeth, magnetotactic bacteria, cuticle and wood, as well as bio-inspired materials like the above mentioned polymer-mineral particles or cellulose based composites were investigated at the µ-Spot beamline. The spatially resolving scanning SAXS/WAXS and XRF (X-ray fluorescence) setup was for example successfully applied to investigate the effect of Strontium ranelate on the formation of human bone **[5]** and the formation of zebrafish fin bone via an amorphous precursor phase **[6]**. The performance of the experimental stage was continuously improved with respect to its resolution, variability of sample environments and the ability to characterize single crystals. This enabled us to study the structure of mercury-thiolate single crystals **[7]** as well as of organic inclusions in biogenic calcite **[3]**. We developed programs for a full 3D reconstruction of the reciprocal space from 2D measurements taken at different angles of rotation (results shown in **Fig. 2**). Furthermore, a method for the local chemical analysis of biomaterials by means of mapping lattice spacings was established **[8]**. A program for online data analysis is currently being developed in cooperation with DESY (Hamburg). The possibility to perform a fast data analysis is expected to have a major impact on future activities at the µ-Spot beamline.

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Advanced Raman Spectroscopic Imaging of Biological Tissues

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Thesis title: Application of innovative techniques for the study of deterioration pathways within objects of cultural and artistic interest
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Biological materials, such as wood or bone, are structured in a hierarchical way over many length scales. **[1]** Conventional single point Raman spectroscopy is inadequate to describe the chemical information and orientation distribution in relation to the macroscale. The focus of our research is *in-situ* studies of biological tissues at various hierarchical levels of structure (from molecular to tissue scale) taking advantage of advanced Raman imaging techniques. One of the goals of our work is to map collagen fibril orientation in tissues by evaluating the molecular response within the tissue to a polarized laser source (**Fig. 1**) **[2]**.

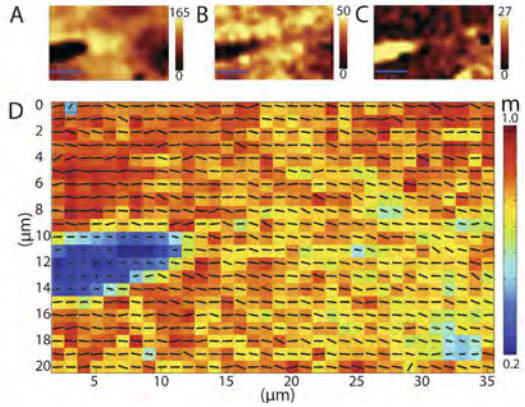

Fig. 1: Polarized Raman mapping of the collagen fibril orientation in mouse bone. The top images show chemical distribution of mineral (A), collagen (B) and embedding material (C) respectively. (D) Collagen orientation map obtained by fitting 13 Raman images collected with different polarization angles of the incident laser light. The direction of lines indicates the orientation of collagen fibrils, their length as well as the color code are related to the amount and three-dimensional organization of collagen molecules.

We are applying this methodology to investigate the evolution of collagen organization in hard and soft tissue formed in fracture gap (callus) during the process of fracture healing in rat bone (with J. Dunlop, Biomaterials, and G. Duda, Charité Hospital Berlin).

The main aim of our work is to link the structural organization and chemical composition to the physical properties of the biological material. One example is a collaboration with M. Harrington (Biomaterials) and J.H. Waite (University of California, Santa Barbara) where we used Raman spectroscopic imaging to study mussel byssal coating and plaque showing micron level spatial distribution of various proteins and their interaction with iron ions (**Fig. 2**) **[3, 4]**. One of the outcomes is that the unique mechanical performance of byssus coating is influenced by the specific distribution of protein-iron cross-links in locally concentrated areas.

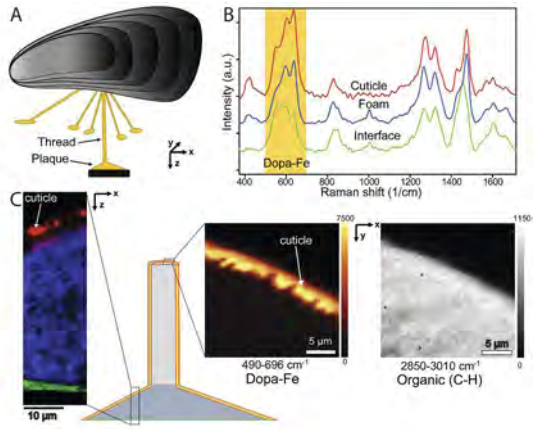

Fig. 2: Raman imaging of Mussel byssus thread and plaque. (A) Mussels produce a holdfast known as a byssus which is composed of extensible and shock absorbing byssal fibers. (B) Average Raman spectra of three morphologically distinct domains in byssus i.e. cuticle, foam, and plaque-substrate interface. (C) Raman images of plaque (left) and thread (right) cross-sections. In the plaque image the distribution of average spectra shown in B is visualized through least square fitting. In the thread images Raman band integrals of dopa-Fe (490-696 cm^{-1}) and overall organic content (2850-3010 cm^{-1}) are shown. Protein-Fe coordination cross-links in the thread result confined to the cuticle region.

Additionally, in collaboration with BAM (I. Rabin) and BESSY (U. Schade), we work on damage assessment of the Dead Sea Scrolls. Combining far infrared and polarized Raman spectroscopy we try to define markers related to changes in collagen molecules caused by deterioration **[5]**.

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Nanometer and Micrometer Studies of Human Teeth and Relations to Dental Restorations

Human teeth do not re-grow, remodel or heal. Yet they function under cyclic mechanical load for many years in the harsh environment of the mouth. It may be hypothesized that the subtle variations observed in the microstructure of dentine and enamel – significantly contribute to the long term durability of human teeth. Understanding the details of the microstructure is therefore of great potential interest for new materials inspiration and design, and also for understanding failure in conventional dental treatment **[1]**. Our work centres on imaging wet human teeth by 2 dimensional (surface) and 3 dimensional (3D, volume) X-ray measurement methods: tomography, diffraction and small-angle scattering. We study the relations between the nanometre-sized carbonated apatite particles and the whole tooth structures (**Fig. 1**) **[2, 3]**. These findings we can now relate also to the 3D distributions of the dominant micrometer sized features of dentine, the dentinal tubules **[4]**. We have seen for instance that the mineral particles change their average orientations on the flanks of teeth and on the chewing surfaces, and that they also re-arrange from being randomly orientated to being more highly aligned in regions beneath the cusps. This suggests a design on the nanometre length-scale that matches the millimetre to centimetre length-scale structure and function of teeth.

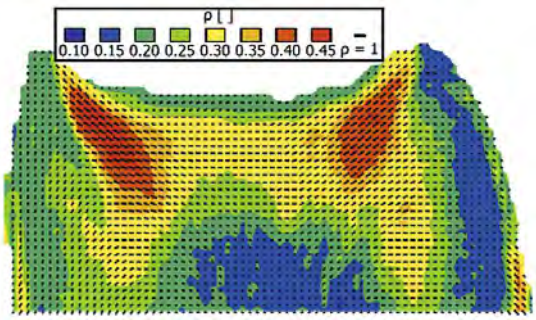

Fig 1. Collagen protein fibres in dentine of teeth are reinforced with tiny apatite particles. The orientation of these 2-4 nm thick particles, as seen by small angle X-ray scattering [2, 3] reveals an arrangement that appears to match and support load under the cusps (indicated in red in the upper left and right regions of the dentin silhouette. ρ represents the degree of co-alignment of the particles in a volume of about 50×50×150μm^3 and is zero for random distribution and is one for regions where particles are fully co-aligned).

Teeth have an important long-term mechanical functional role, and even if they are infected, they are often restored back into function. Imaging the microstructures of teeth and dentine are of particular potential use in benefitting clinical dentistry problems of matching fillings to the tooth microstructures. Indeed, the margins of fillings and restorations are key determinants for the quality of dental treatment, providing some measure of the ability of restorations to function for extended periods of time in the mouth **[1]**. However, it remains unclear to what extent leakage and bad fittings of restorations indicate failure and the need for new treatment. A growing availability of new phase-imaging methods allows us to investigate the interfaces between teeth and restorations **[5]** and to better observe and measure regions where the biomaterials should create durable interfaces with the natural tooth tissues (**Fig. 2**). These methods are also being used in basic studies such as the investigation of molar teeth of the crayfish Cherax quadricarinatus.

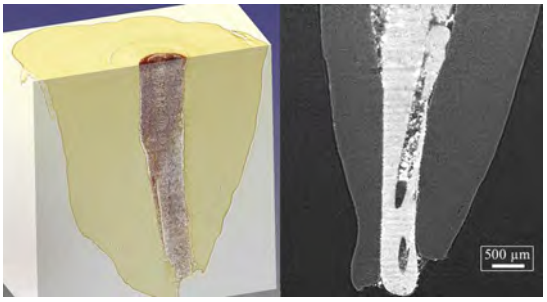

Fig 2. Root canal therapy with details revealed by phase-contrast enhanced micro tomography. A 3D representation (left) and 2D slice through the data (right), reveal what may be seen in a typical human root (root appearing in yellow) that is filled with dense conventional silver-containing filling/cement biomaterials (depicted in orange). The virtual data is vertically sliced so as to visually expose the internal structures. Although densely packed by an expert dentist, the filling biomaterials contain voids and inhomogeneities, with visible discontinuities near the dentine [5]. Gaps and unfilled regions spanning less than 20 micrometers can be seen in such fillings, and they have important but still unconfirmed clinical significance for long-term success.

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1991-2000: Clinical dentistry in public and private clinics
2000-2005: PhD, Chemistry (Weizmann Institute of Science, Rehovot, Israel)
Thesis: Human Tooth Structure-Function Relations: a Study of Mechanisms of Stress Distribution During Mastication
Since 2005: Researcher (Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany)

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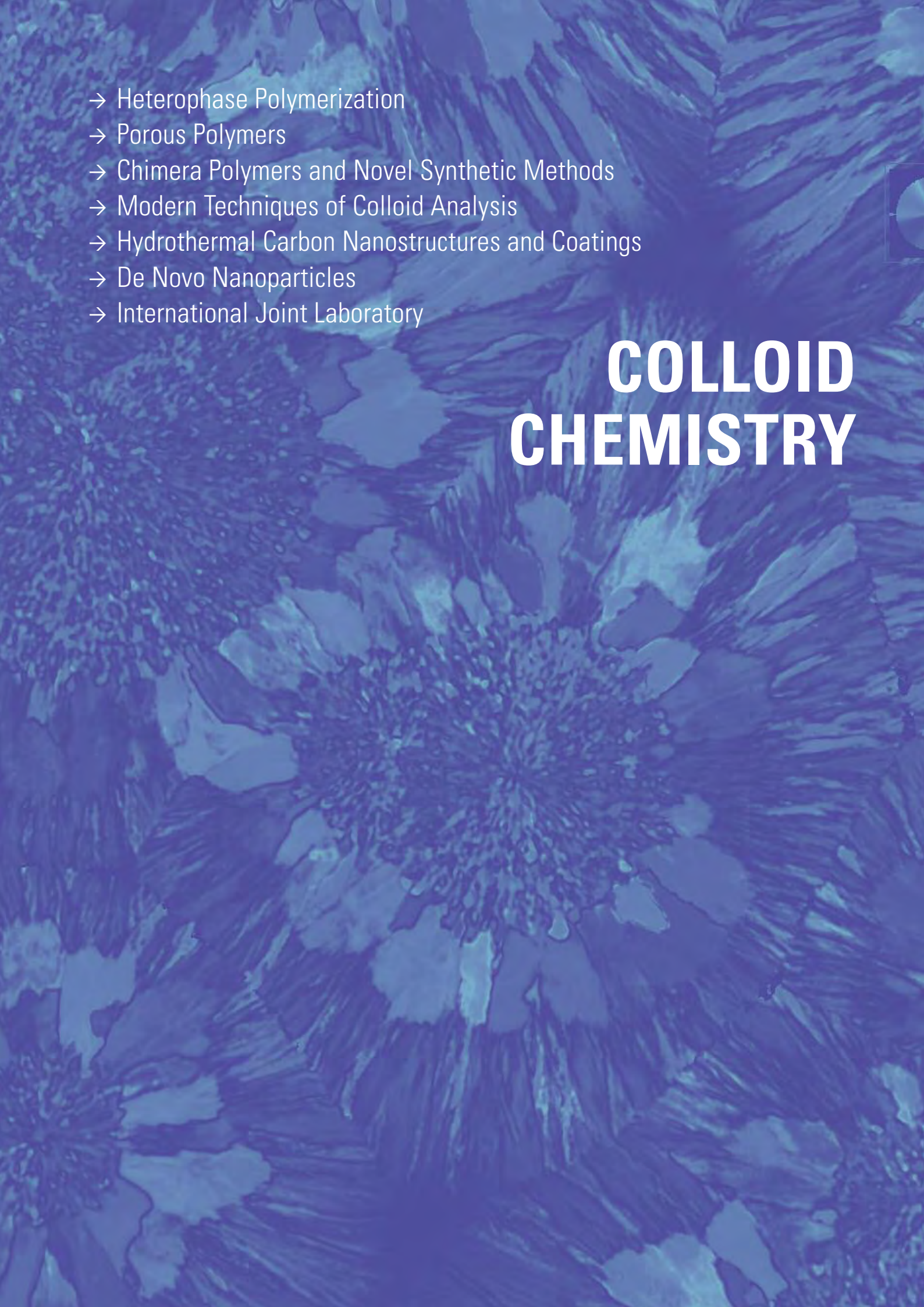


- → Heterophase Polymerization
- → Porous Polymers
- → Chimera Polymers and Novel Synthetic Methods
- → Modern Techniques of Colloid Analysis
- → Hydrothermal Carbon Nanostructures and Coatings
- → De Novo Nanoparticles
- → International Joint Laboratory

COLLOID CHEMISTRY

Research in the Department of Colloid Chemistry

Markus Antonietti 06.02.1960
1983: Diploma, Chemistry (University of Mainz)
Thesis: Bestimmung der Diffusion von photomarkiertem Polystyrol: spezielle Systeme, chemische und physikalisch-chemische Aspekte
1985: Doctorate for natural science (summa cum laude, University of Mainz
Thesis: Diffusion in topological constraint polymer melts with Prof. Dr. H. Sillescu
1990: Habilitation, Physical Chemistry (University of Mainz) Thesis: Microgels – Polymers with a special architecture
02/1991: Associate Professor (University of Mainz)
09/1991: Full Professor (Philipps University Marburg)
Since 1993: Director (Max Planck Institute of Colloids and Interfaces, Golm),
Full Professor (University of Potsdam)

Scientific Profile

The size of the Department of Colloid Chemistry is currently about 60 people, with 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 further "drain" of 2 group leaders in the period ahead, reconstruction of the department went on and was most serious. Dr. Helmut Cölfen, left for Full professorship to the University of Konstanz, and the Emmy Noether group of Dr. Hans Börner now turned into a Full Professorship at the HU Berlin. This was followed by the leaving of a set of key Post-Docs towards permanent international positions, which complemented the drain. The just recently established groups of Dr. Maria Magdalena Titirici on "Hydrothermal Carbon", Dr. Cristina Giordano ("De Novo Nanoparticles"), and Dr. Xinchen Wang ("Artificial Photosynthesis") are now complemented by another two fresh group leader, Dr. Jens Weber ("Porous Polymers") and Dr. Jiayin Yuan (Polymeric Ionic Liquids, starting from 2011). 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
· Chimera Polymers and Novel Polymerization Techniques
· Modern Techniques of Colloid Analysis
· Materials for Energy applications
· Hydrothermal Carbon Nanostructures and Coating
· New inorganic nanostructures
· 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, foams) by a rational use of the particle interfaces in heterophase polymerization *(Dr. Klaus Tauer)*.

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)*.
. A new organization principle based on two immiscible, both water soluble blocks was identified. These double hydrophilic block copolymers enable the separation and self organization of two aqueous entities *(Dr. Helmut Schlaad, with Markus Antonietti)*
· The performance of molecular drugs or diagnostic particles 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 nanoparticles is used in cooperation with pharmaceutical/medical partners to generate tailor made colloidal diagnostica *(Dr. Cristina Giordano, together with the Seeberger department)*.

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

Due to the promotion of some of the previous group leaders, headhunting of young scientists in area is requested to keep the analytical strength also within the department. This however is an ongoing operation.

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, especially in electrocatalysis and fuel cell applicaitons *(Dr. Jiayin Yuan, Markus Antonietti)*

· Porous tectonic polymers as membranes for fuel cells and battery separators and as novel gas storage materials *(Dr. Jens Weber)*

Hydrothermal Carbon Nanostructures and Processes

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 useful 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

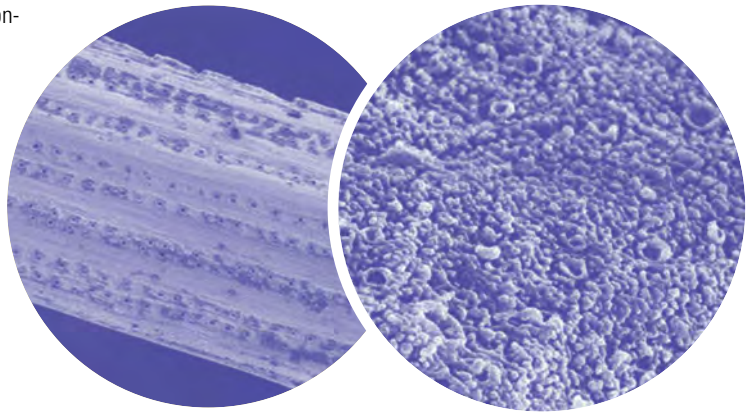
In spite of the fact that nanoscience is a rather mature discipline, it is astonishing that the width of easily accessible nanostructures is still rather small, i.e. most experiments are done with a very restricted set of chemical systems, such as Au or CdS. Many materials which are relevant for novel energy cycles and to catalyze more efficient chemical reactions simply do not exist as appropriate nanostructures, or their synthesis is highly non-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:

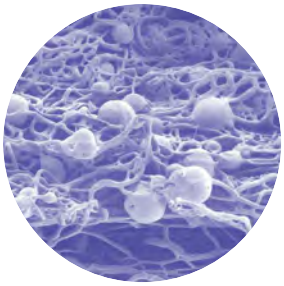
. Metal carbide and nitride particles offer new pathways for metal/base catalysis, but also are record holders in mechanical hardness or magnetization *(Dr. Cristina Giordano)*.

· This is also true for the corresponding metal borides and boronnitrides, which are new land for chemistry, when rational nanostructures are to be made *(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. Maria Magdalena Titirici)*.

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





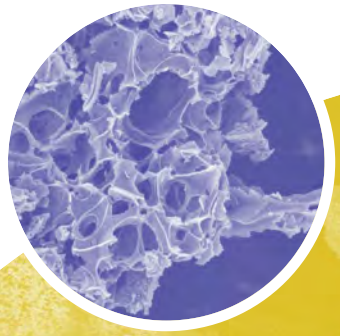
Artifical Photosynthesis
This international joint laboratory was established in July 2008 between the Max-Planck Institute of Colloids and Interfaces and Fuzhou University. Natural photosynthesis, the process by which green plants are converting solar energy into chemical energy, has inspired the development 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.

Our group investigates a new class of 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 a set of new reactions for 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. The gained scientific results from this cooperation are indeed more than only promising.

The previously 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 six years clear visibility and 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 internation



alization of our relations. Beside the well established Partner group at USCT/Hefei, we started a virtual "Artifical Photosynthesis Center" with the Fuzhou University, and establish an Exchange Program with Kyushu University. With the Thailand Nanocenter (NSDEC), we plan a massive program on "Nanoscience for Agriculture"

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,
· GC- and LC-mass spectrometry,
· FT-ATIR for liquid analysis.

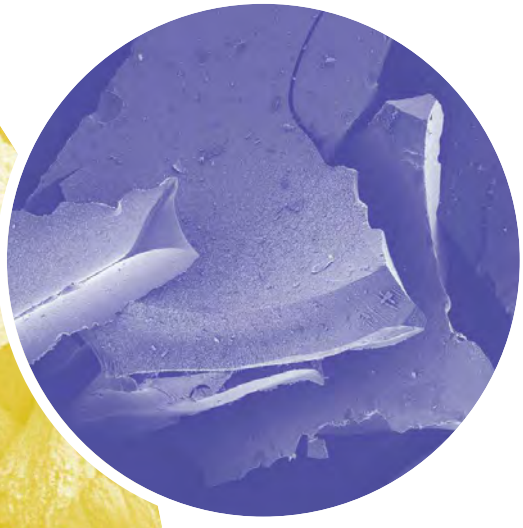
One of the labs, the electron microscopy lab, is a so-called "central service labs", i.e. it belongs and is operated by the department, but is also designated to perform scientific routine measurements for the whole institute. All other instrumental labs are not devoted to service operations, but are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

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 and Firmenich. 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 2009, I received the Gold Medal of the UK Polymer group, which is a distinction for lifetime achievements, in 2011 I will receive the Binational Price for promoting French-German Scientific Cooperation.

Markus Antonietti,
Director of the Department
of Colloid Chemistry



Polymer Dispersions/Heterophase Polymerizations

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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)
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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

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Latex Crystals [1]

Monodisperse latexes form in gravitational fields highly ordered regions of fcc-lattice type. If the spacing of the lattice planes (d_{hkl}) is in the proper range, angle-dependent color effects are observed (**Fig. 1**).

Bragg reflection is detected perpendicular to the lattice planes for first order reflections if the condition $d_{hkl} \approx \lambda_0/(2 \cdot n_D)$ is met. d_{hkl} is the lattice spacing, λ_0 the wave length of the Bragg peak, and n_D the refractive index. The surface distance between the particles is given by $d_{PP} = d_P \cdot \sqrt[3]{0{,}74/\Phi_P} - d_P$ and the center to center distance is $D = \sqrt{3/2} \cdot d_{hkl} = d_{PP} + d_P$.

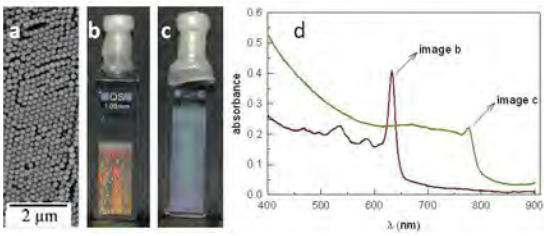

Fig. 1: SEM image (a), snapshots of a crystallized latex at high (b) and low (c) ionic strength, and their absorption spectra (d); d_p=229 nm

UV-Vis spectroscopy allows the determination of d_{hkl} and if the particle size and packing order are known, d_{PP} is accessible. A modified DLVO theory, with the assumption of a non-isotropic distribution of the ionic strength in the continuous phase, can be used to study the ordering of latex particles. It leads to an energy barrier counteracting the gravitational force and keeping the particles at distances which are in good agreement with the d_{PP} values estimated from UV-Vis measurements (**Fig. 2**).

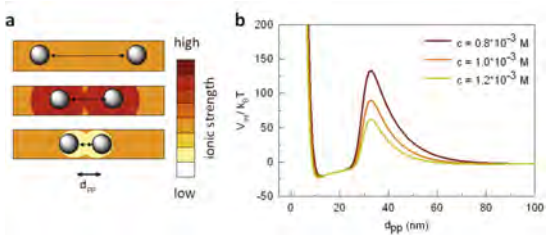

Fig. 2: Schematic illustration of non-isotropic ionic strength (a) and calculation results showing the appearance of an energy barrier counteracting gravity for varying concentration of 1:1 electrolyte (b)

Latex Particles with Special Morphology [2, 3]

Typically latex particles are of spherical shape surrounded by a hairy layer of less than 10 nm thickness. The origin of this layer is the hydrophilicity of the stabilizing groups which are attracted by the aqueous phase pulling neighboring carbon atoms away from the hydrophobic core. The greater is the chain length of the stabilizing polymers the lower their surface concentration. The morphology of such polystyrene particles (PS) stabilized by poly(ethylene glycol) (PEG) with a molecular weight of one million g/mol is very special (**Fig. 3, 4**). These particles are composed of triblock copolymers synthesized by ordinary radical heterophase polymerization. The radicals are generated via redox-reaction with ceric ions at the PEG chain ends that initiate polymerization of N-isopropylacrylamide (NIPAM). These diblock copolymers precipitate at the polymerization temperature of 60°C thus generating the reaction sites for the subsequently added hydrophobic monomers.

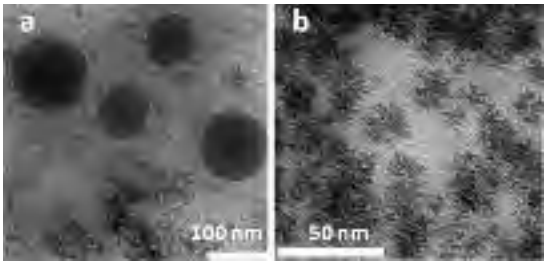

Fig. 3: TEM images showing the precipitation structure of PEG with an average molecular weight of one million (a) and diblock copolymer of PEG-PNIPAM as obtained after the first stage of the polymerization (b)

The morphology of the diblock PEG-PNIPAM precipitation structures looks bicontinuous as darker and brighter regions alternate and their size is quite monodisperse. The PEG-PNIPAM-PS triblock copolymer particles are of spherical shape and both the SEM and TEM images reveal a peculiar surface morphology (**Fig. 4**).

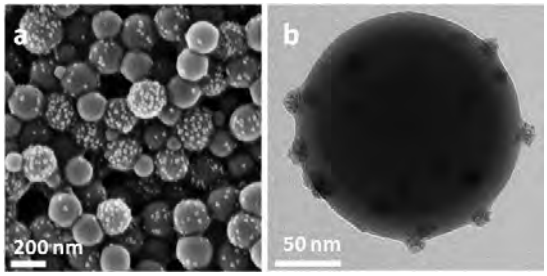

Fig. 4: SEM (a) and TEM (b) image of PEG-PNIPAM-PS triblock copolymer particles

The surface of the particles looks like sprinkled with buds of uniform size between 18 and 20 nm, but the number of (visible) buds per particle differs greatly. The size and shape of the sprinkles is alike the precipitation structure of the PEG-PNIPAM diblock precursor copolymer (image b of **Fig. 3**).

Distimuli-Responsive Block Copolymers [3, 4]

Block copolymers made of PNIPAM and poly(1 - (2 – acryloyloxyundecyl) – 3 –methylimidazolium bromide) which is an

ionic liquid polymer (PIL) are di-stimuli-responsive i.e. the PNIPAM block reacts on temperature changes and the PIL block on the concentration and nature of the counterions (**Fig. 5**).

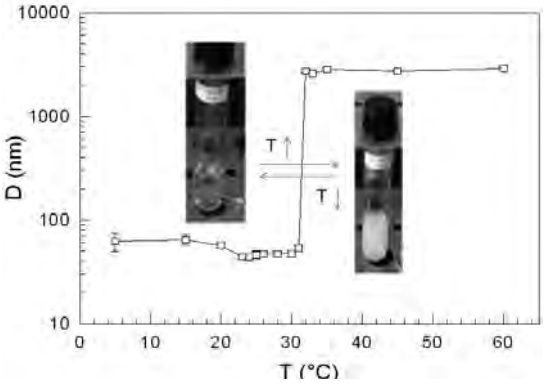

Fig. 5: Particle size (D) evolution of PIL-PNIPAM block copolymer in dependence on temperature showing the transition from solution to suspension at 60°C due to precipitation of the PNIPAM block

The PNIPAM block is hydrophilic below and hydrophobic above 60°C. Above this temperature macrophase separation leads to particles having PNIPAM cores and stabilizing PIL corona.

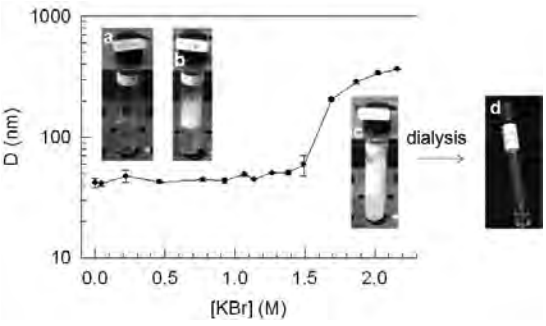

Fig. 6: Particle size (D) evaluation of PIL-PNIPAM block copolymer in dependence on KBr concentration showing the transition from solution to suspension, image (d) shows that the process is reversible if the excess KBr is removed by dialysis

The anion sensitivity of the PIL block is proven by the addition of KBr (**Fig. 6**). The diblock condenses above a certain Br^- concentration. In this system, while the PIL block is condensed, the colloidal stability appears provided by a corona of PNIPAM. Both transitions are fully reversible and can be repeated several times.

Composite Microcapsules [5, 6]

The combination of interfacial polycondensation and radical heterophase polymerization in an one pot multi-step reaction is an efficient way to produce composite microcapsules (**Fig. 7**). The first step is the emulsification of the template oil phase (pure styrene monomer or in combination with cyclohexane – chloroform 4:1 mixture), that contains terephthaloylchloride, and the oil-soluble radical initiator in an aqueous poly(vinyl alcohol) solution. In the second step, the polyamide capsule formation is started by the addition of an aqueous diamine solution at room temperature. Then, after one hour, the radical polymerization as third step is initiated by raising the temperature to 60°C.

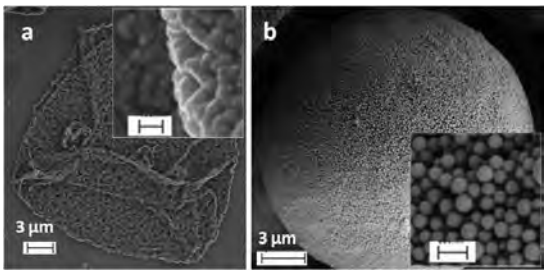

Fig. 7: SEM images of a polyamide (PA) capsule after polycondensation (a) and composite capsule after styrene polymerization (b) initiated with azobisisobutyronitrile; the bar of the insert in (a) and (b) represent 100 and 300 nm, respectively

The radical polymerization is not restricted to the PA capsules' interior but an ordinary emulsion polymerization takes place in parallel (**Fig. 7 and 8**).

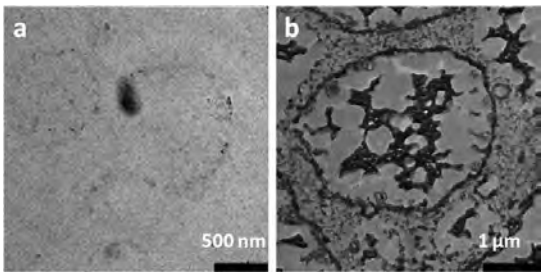

Fig. 8: TEM images of thin cross-sections of embedded PA (a) and composite capsule (b)

The morphology of the composite capsules depends strongly on the amount of styrene monomer in the oil mixture and the nature of the initiator.

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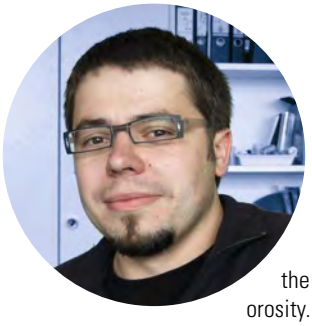
From Polymer Synthesis to Porosity Analysis



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High-Performance Polymers such as aromatic poly(imide)s or poly(benzimidazole)s are an important class of polymers in a variety of applications that are related to energy technologies (e.g. gas separation, fuel cell membranes etc.)**[1]**

These applications can often benefit from the presence of a well-defined meso- or microporosity. Although a lot of progress has been achieved in the synthesis of porous polymers during the last years, there is still a lack of understanding with regard to the stability of such small pores (< 10 nm) in "soft" polymeric materials. Furthermore, the synthetic pathways towards porous high-performance polymers are still limited to classical petrochemical routes, which should be overcome to achieve truly sustainable polymer chemistry.

New Synthetic Pathways

The classic synthesis of aromatic high-performance polymers requires typically the use of high-temperatures and harmful organic solvents such as m-cresol etc. Recently, there was an increased interest in the ionothermal synthesis of polymers and polymer networks. The use of inorganic salt melts (e.g. LiCl/KCl) can be beneficial for the synthesis of polybenzimidazole (PBI), a polymer which requires typically harsh synthetic conditions (use of strong acidic solvents or toxic byproducts such as phenol) **[2]**. Besides molten salts, we are also interested in the use of molten salt hydrates or just plain hot water (hydrothermal synthesis) as effective solvents for polymer synthesis.

Furthermore, we are interested in the use of natural resources (e.g. lignin or birch bark extracts) as monomer resources.

Mesoporous Polymers

Mesoporous polymers, i.e. polymers having pore sizes between 2 and 50 nm, are far less investigated compared to their inorganic counterparts such as mesoporous silica or metal oxides. This is somewhat surprising regarding the high potential of mesoporous materials in a number of applications (e.g. separation science, controlled release, etc.).

We have an interest in both, the synthesis and characterisation of mesoporous polymers. There is still a need to develop new synthetic routines towards mesoporous polymers. Furthermore, the stability of mesopores against collapse as well as the details of pore collapse are widely unexplored. We use gas sorption together with scattering techniques and thermoporometry to analyse mesoporous polymers.

From a synthetic point of view, we focus mainly on the hard-templating pathway, which involves the replication of silica nanostructures, such as nanoparticles.

Recently, this pathway was used for the synthesis of mesoporous polystyrene and polyacrylate gels. **[3, 4]** The cross-linking density of the gels was varied between fully and non cross-linked, which allows a more detailed analysis of the mesopore stability against solvent and temperature treatments.

Fig 1 shows exemplary FESEM micrographs of mesoporous polystyrene (PS) which was subjected to various temperatures. It is obvious that pore collapse sets in already at temperatures well below the nominal glass transition of PS. This is due to the nanosized pore walls which are affected by a lowering of T_g.

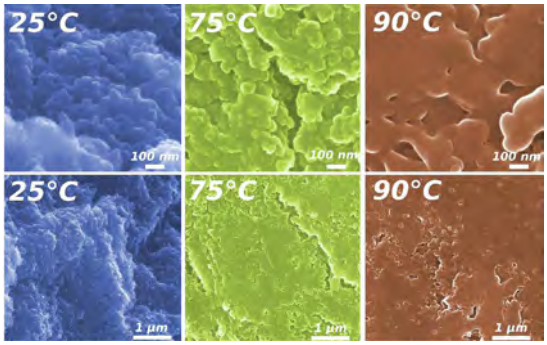

Fig. 1: FESEM images of mesoporous PS subjected to varying temperature. Pore collapse sets in already at 75°C, which is ~25°C below the glass transition temperature of PS

The analysis of the freezing/melting behaviour of solvent which is confined within mesopores can also be used to analyze mesoporous systems (thermoporometry). The phase transition temperatures are lowered due to the presence of highly curved interfaces. This techniques allows the analysis of solvent-swollen systems, such as mesoporous hydrogels (**Fig. 2**). By comparison with dry samples, it could be shown that the pore collapse can be reversible. That is, at low cross-linking degree no porosity is observed in the dry state, but the pores open up again upon solvent treatment. The results of SAXS analysis were consistent with the thermoporometry results.

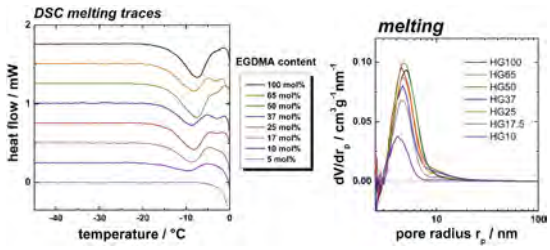

Fig. 2: DSC melting traces (left-hand side) of water confined within mesoporous hydrogels with varying cross-linker degree and the respective pore size distributions (right-hand side)

Microporous Polymers

Microporous Polymers are of high interest, both from an academic and commercial point of view. They could find applications in gas separation/storage, sensor or optoelectronic applications.

The analysis of soft microporous matter was however not developed at the same pace as the synthesis. This might be due to the main problems associated with the analysis of soft, amorphous matter: swelling and deformation effects.

We are interested in the synthesis and characterization of both: cross-linked and non cross-linked microporous polymers. Characterization is mainly performed on the basis of gas sorption, using various probes (nitrogen, argon, carbon dioxide and hydrogen). The results are cross-checked by additional methods like X-ray scattering and NMR-techniques.

In this way it is possible to overcome problems associated with the use of nitrogen sorption alone, such as slow kinetics, liquid plugs etc.

As an example, we analyzed intrinsically microporous polyimides in dependence of their molecular geometry and the processing (precipitation vs. solution casting). **[5, 6]** Carbon dioxide and hydrogen can reliably probe much smaller pores than nitrogen. Hence, it was possible to determine the limits of intrinsic microporosity with regard to molecular properties (chain geometry and flexibility) in more detail. Only polymers that are not capable of adsorbing H_2 and CO_2, can be regardded as truly non-porous (non-connected and non-accessible free volume). Additionally, the influence of processing can be analyzed (**Fig. 3**). By that, significant differences of the applied methods (such as different analysis temperatures) became obvious. These effects need more clarification within the next years.

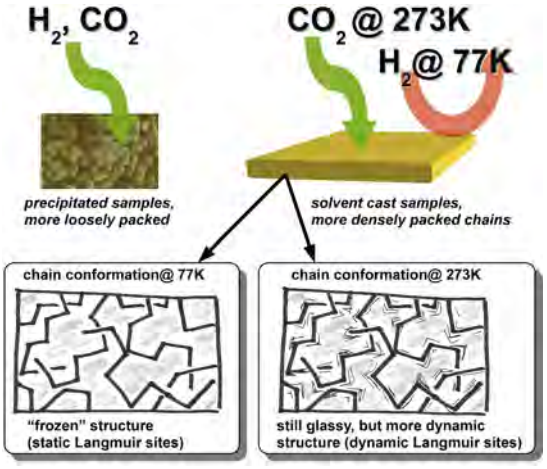

Fig. 3: Overview on the observed differences in gas uptake of microporous polyimide upon different processing (upper part) and sketch of the underlying temperature dependent microstructure

Another example is a case study on microporous networks, which had the intention to identify reliable methods for the extraction of important parameters (specific surface area, pore size and volume) from gas sorption and ^{129}Xe-NMR data.**[7]** Swelling effects could be clearly identified and their impact on the determination of the pore size distribution was analyzed. A major result of these studies is the dynamic character of the micropores. It seems quite likely that they can adopt their pore size by elastic deformations to their environment (dry atmosphere, solvent filled, etc.). This has severe implications on the application of such materials.

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Bioinspired Polymers and Colloids

Biohybrid copolymers are interesting materials for the bioinspired generation of "smart" functional colloids and hierarchical structures, for usage in for instance life science applications. Advanced new materials (polypeptides, pseudopeptides, glycopolymers, etc.) are prepared by controlled polymer synthesis techniques and studied according to their complex or higher-order self-assembly in solution or in solid state.

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Synthesis

Radical thiol-ene ("click") photochemistry has been applied to the modification of well-defined copolymers based on polybutadienes **[2]**, polyoxazolines **[1, 4]**, and polypeptides **[13]**. In addition, the concept has been extended to the heterophase functionalization of polymer colloids **[7]** and inorganic surfaces, i.e. glass fibers and slides (**Fig. 1**) **[8, 10]**. Particular emphasis was put on the preparation of sugar-containing materials.

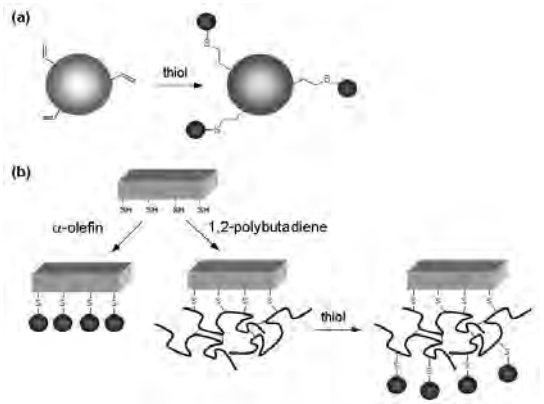

Fig. 1: Schematic illustration of the heterophase thiol-ene functionalization of (a) colloids and (b) surfaces.

Polymer Self-Assembly

Glucosylated polybutadiene-poly(ethylene oxide) (PB-PEO) block copolymers formed very large vesicles of greater than 500 nm in diameter by direct dissolution in water. The existence of unilamellar vesicles could be confirmed by light scattering analyses (DLS/SLS) and transmission electron microscopy (TEM). Chains can only be packed in a monolayer, accordingly these vesicles should have an asymmetric membrane with different hydrophilic layers on the outside and on the inside (**Fig. 2a**). 2D-NOESY-NMR experiments indicated that the glucose (Glc) units are spatially separated from the PEO chains (**Fig. 2b**), and surface-enhanced Raman spectroscopy provided evidence that glucose is located on the outside and PEO on the inside **[2]**.

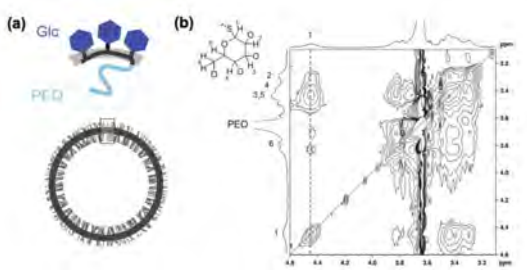

Fig. 2. (a) Schematic illustration of a glycopolymer vesicle with an asymmetric membrane and (b) 2D-NOSY-NMR spectrum (500 MHz) of glucosylated PB-PEO block copolymer vesicles in D_2O; the missing cross peak between Glc CH and PEO indicates spatial separation of the two hydrophilic moieties.

Poly[2-(4-(β-D-glucosylsulfanyl)-butyl)-2-oxazoline] in water formed nanotubes measuring several hundreds of nanometers in length, as observed by scanning force microscopy (SFM). The diameter of the tubes was found to be 4–9 nm, and the thickness of the wall was about 1 nm (small-angle X-ray scattering, SAXS). Formation of the tubes should occur via a 2D hydrogen-bonded layer of interdigitated polymer chains undergoing bending and closing to a tube. Supporting the idea of a hydrogen-bonded structure, the nanotubes were not observed in 8 M aqueous urea or in PBS buffer solution **[4]**.

Poly(2-isopropyl-2-oxazoline) (PIPOX) homopolymers can be crystallized in hot aqueous solution at a temperature above the cloud point temperature, producing uniform microparticles with internal fibrous structure (**Fig. 3**) and a melting point close to 200°C. It was proposed that hydrophobic and oriented dipolar interactions promote a slow crystallization of chains to form nanoribbons, which then fuse together to form nanofibers. These nanofibers assemble into microspheres, which, however, could be suppressed by the presence of small amounts of a co-solvent (e.g. ethanol or tetrahydrofuran) or surfactant (e.g. sodium dodecylsulfate) **[11, 16]**.

The kinetics of the crystallization process and time-dependent evolution of the morphology were studied using wide-angle X-ray scattering (WAXS) and cryogenic/conventional scanning electron microscopy (SEM). The results indicate that the temperature-induced phase separation of dilute aqueous PIPOX solutions produced a bicontinuous network-like structure (**Fig. 4a**). With the onset of crystallization after ~4 h (for 1 wt% PIPOX in water at 60 °C) the network collapses into individual particles composed of a porous fiber mesh. These "premature" particles then act within the next ~5 h as nucleation sites for secondary crystallization. Nanofibers preferentially form at the particle surface, thus wrapping the microspheres like a ball of wool (**Fig. 4b**). This stage is characterized by a steep increase in the crystallinity of the material. Crystallinity reaches a plateau after 8-10 h, when most of the amorphous material is depleted. At this time, compact and isolated microspheres of uniform size have been formed **[14, 16]**.

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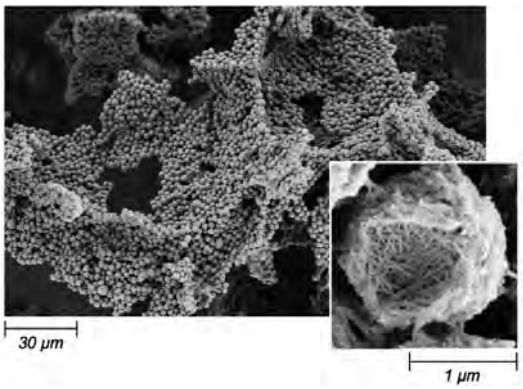

Fig. 3: Scanning electron micrographs of crystalline PIPOX microparticles with hierarchical structure.

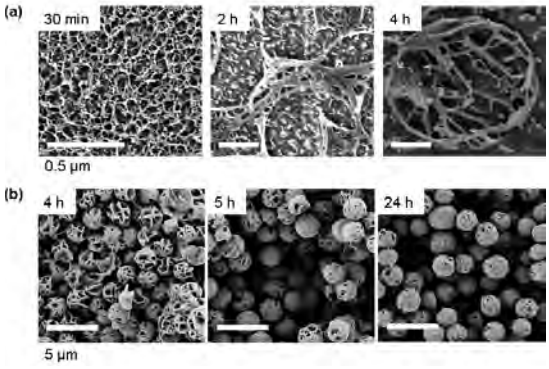

Fig. 4: Evolution of the morphology produced during the annealing of a 1 wt% aqueous solution of PIPOX as visualized by (a) cryogenic SEM (t ≤ 4 h) and (b) conventional SEM (t ≥ 4 h); the onset of crystallization occurred at t ~ 4 h (WAXS).

Biofunctional Colloids and Surfaces

Glycosylated microspheres were obtained by the crystallization of poly[2-(isopropyl/3-butenyl)-2-oxazoline] (5 mol-% of unsaturated units) from aqueous solution above its cloud point, followed by the covalent attachment of 1-thio-β-D-glucose or galactose using thiol-ene chemistry (60% conversion of double bonds). The carbohydrate moities on the surface selectively interacted with lectins and the microspheres could thus be employed as "fishing rod" for the isolation and separation of specific lectins, i.e. ConA and RCA I, from a mixture (**Fig. 5**) **[7]**.

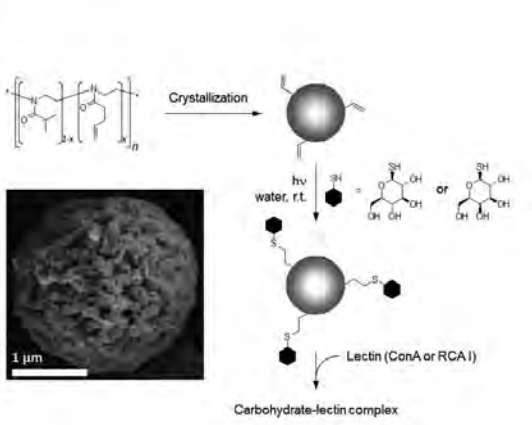

Fig. 5: Preparation of polyoxazoline-based crystalline microspheres for carbohydrate-protein (lectin) recognition; image shows the scanning electron micrograph of a freeze-dried glucosylated microsphere.

Sulfhydrylated glass slides were functionalized with 1-allyl-α-D-glucopyranoside and analyzed according to the ability to selectively bind to the lectin Con A **[8]**. For this purpose, glucose-coated glass slides were incubated with a solution of fluorescent Con A, and the interaction between the sugar units and the lectin were monitored by fluorescence microscopy. The degree of lectin binding was rather low, but could be considerably increased upon inclusion of a flexible polymer layer (**Fig. 1b**).

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Electron Microscopic Studies of Colloidal Systems and Biomaterials

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The study of structure/property, structure/function and chemical synthesis/structure relationships of both natural and synthetic colloidal and biological materials is one of the main topics of the research at the MPI of Colloids and Interfaces. Hierarchical structured biological and biomimetic materials and hybrid materials, active coatings and interfaces, functional supramolecular organizates, the synthesis of bio-inspired polymers, novel synthetic inorganic nanoparticles and organic-inorganic hybrid materials, porous polymers, functional carbonaceous materials and the synthesis polymer particles are in focus on the interdisciplinary research in the institute. Transmission, high-resolution scanning and environmental electron microscopes are powerful tools to investigate the morphological ultra-structure with a high electron optic resolution. The electron microscopy lab is a so called service lab to perform scientific routine measurements for the whole institute. Some selected interesting results are presented here.

Controlled nanoparticle aggregation is a topic of our scientific interest. The nanoparticle aggregation based growth of calcite crystals, which can be tuned by regulating the concentrations of calcium ions and the polyelectrolyte additive in aqueous solutions. Using the random copolymer polyelectrolyte poly(4-styrene sulfonate)-*co*-(maleic acid) (PSS-*co*-MA) considerably guides crystallization of calcium carbonate (CC) with a high versatility. The bio-inspired non-classical crystallization protocol yielded a series of calcite microstructures. Simple variation of calcium and polyeletrolyte concentrations enables a systematic control over the size and morphology of particles among pseudo dodecahedra, pseudo octahedra, multilayered spheres and hollow spheres **[1]**. In order to gain more insight into the formation of calcite pseudo dodecahedral single crystals, the particles obtained at a much lower PSS-*co*-MA concentration (2.5 mg/L) but the same $CaCl_2$ concentration (1.25 mM) was characterized by high-resolution scanning electron microscopy (HRSEM). As shown in **Fig. 1**, the intermediates obtained after 1 week are microparticles with different shapes. We also attempted to evoke shape control by face selective polymer adsorption after introducing foreign seeds at the start. The seed for the shape conversion process was chosen to be rhombohedral calcite particles. When PSS-*co*-MA of 0.1 g/L was used as the aqueous solution medium for the morphogenesis, only slight truncation at edge sites was observed. Using a mixture of PSS-*co*-MA and $CaCl_2$ of 1.25 mM, the resultant crystals became larger in size with time indicating particle growth (Fig. 1c) and displayed sleek edges after 2 weeks.

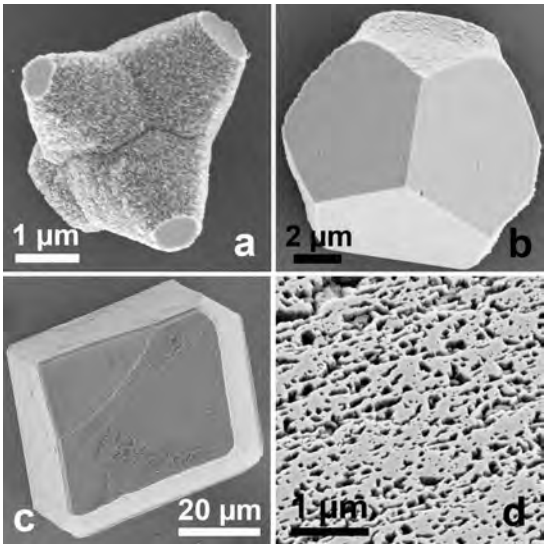

Fig. 1: Calcite particles with curved rhombohedral surface shape (a) and pseudo dodecahedral shape (b), rhombohedral calcite particle (c) with etching pits on {104} faces (d)

These edges were formed by face selective polymer adsorption while the {104} faces also show etching pits (**Fig. 1d**) through irreversible dissolution. Rhombohedral calcite single crystal seeds in a growth solution containing the polymer do not produce pseudo dodecahedral morphology but a rhombohedron with truncated edges due to face selective polymer adsorption in a classical growth process.

One interesting subject is the crystallization of polymers from solution induced by liquid-liquid phase separation. In order to clarify the crystallization mechanism and to elucidate the evolution of the formed spherical morphology, the crystallization of the thermo-responsive poly(2-isopropyl-2-oxazoline) (PiPOx) in aqueous solutions by systematic variation of temperature and polymer concentration **[2]**. Upon

heating e.g. a clear 1 wt.-% aqueous PiPOx solution above the cloud point phase separation takes place. After annealing the system at 60°C freeze-dried samples were investigated by HRSEM. The droplet-like particle morphology obtained after 3 h (**Fig. 2a**) at 60°C showed closed surface structure. However, after 4 h annealing, the morphology considerably changed (**Fig. 2b**). The spherical and rather porous particles have a diameter of around 2 µm, whose framework shows a fibrillar structure. Besides, bending layers of fibers and hollow hemispheres are observed. These premature particles did not grow in size but the cavities became smaller until compact, isolated particles of regular size and shape was obtained (**Fig. 2c,d**). However, the general morphology was maintained at longer times of annealing and the structure appeared to be stable over time. This might be used to tune the properties of the crystalline microspheres for various applications, e.g. in chromatography.

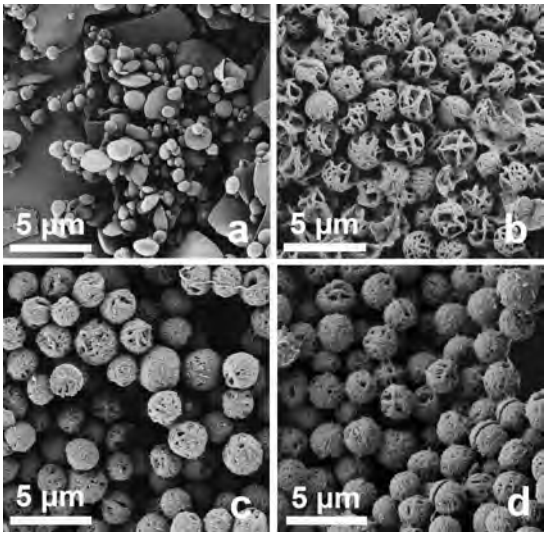

Fig. 2: PiPOx Particles grown for 3 h (a), 4 h (b), 24 h (c) and 120 h (d).

Another interesting project is the electron microscopic characterization of microporous and mesoporous carbon materials formed by template-free preparation of dicyanobi - phenyl (DCBP). The influence of the experimental conditions (salt/monomer ratio, temperature, heating rate) for the DCBP monomer to understand and adjust mesopore formation was studied **[3]**.

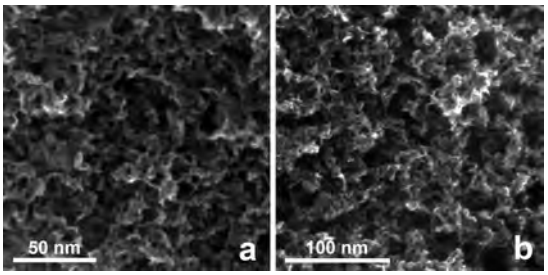

Fig. 3: Mesoporous structures prepared from DCBP with 5 (a) and 10 (b) equivalents of $ZnCl_2$

The ionothermal polymerization of DCBP in an excess of $ZnCl_2$ at 400°C produces an amorphous material with high surface area and micropores of the order of 2 nm in size. Mesopores are formed at a higher reaction temperature (600°C) in addition to micropores. The shape of the nitrogen adsorption-desorption isotherms completely changes from 2 to 20 equivalents of salt, reflecting an extreme increase of the size of the mesopores. A formation of larger pores is presumably due to the onset of phase separation between the forming carbonaceous polymer and the salt phase. As phase separation should have an influence on the morphological structure, HRSEM investigations were carried out (**Fig. 3**).

The prepared materials are highly homogeneous and macroscopic heterogeneities are absent on all scales. Samples prepared from DCBP at 600°C with 5 equivalents of $ZnCl_2$ constist of mesopores with sizes of up to 5 nm and an interconnected, droplet-like porosity (**Fig. 3a**). Bigger pores (>10 nm) of the material are formed by using 10 equivalents of $ZnCl_2$ (**Fig. 3b**). Such morphologies are similar to those of gels obtained from spinodal demixing and favorable for transport and permeation.

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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 aspirates 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.

a) Nanostructured Carbon Materials

Carbons (glassy carbons, activated carbons, coals, porous graphitic carbons) have been used by mankind since many years and they touch every aspect of our daily lives. 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, being a green and cheap method to directly produce spherically shaped functional carbon from carbohydrates (**Fig. 1**) **[1, 2]**. The reaction mechanism for the formation of the carbon spheres involves the dehydration of the carbohydrate in the first step and subsequent polymerization and carbonization of the so-formed organic compounds in the second step **[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.

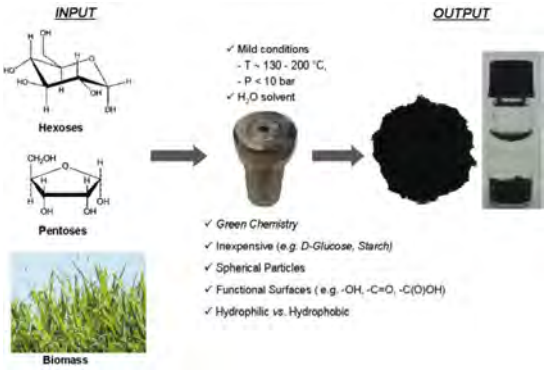

Fig.1: Hydrothermal carbonization process

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 or alumina (as hard templates) or block copolymers or latexes (as soft templating) **[6, 7]** followed by removal of templates, mesoporous functional hydrophilic carbons materials are easily obtainable (**Fig. 2**). 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.

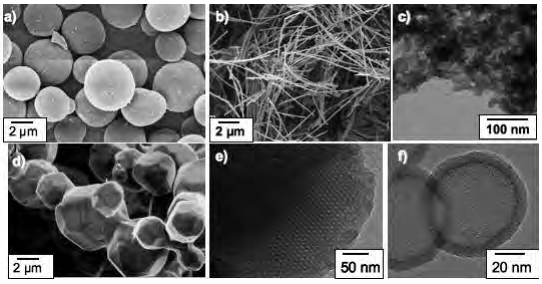

Fig.2: Nanostructured hydrothermal carbonaceous materials: a) mesporous carbon spheres obtained via HTC in the presence of nanostructured silica templates; b) tubular carbon obtaining via HTC in the presence of macroporous alumina membrane; c) carbon aerogel from glucose in the presence of borax; d) e) mesoporous carbon obtained via HTC of fructose in the presence of pluronic F127 block copolymer f) hollow carbon spheres obtained using HTC of glucose in the presence of latex nanoparticles

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. We are currently investigating the mechanism of the HTC process of rye straw in comparison with pure carbohydrates and the important factors which influence it **[8]**. Biomass conversion is a meaningful way to transfer biomass into useful materials, more efficient energy carriers and/or carbon storage deposits. Transfer of biomass towards carbon rich, coal-

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like derivatives is one option to sequester carbon and the stored energy from plant material. This represents also an efficient process to remove atmospheric CO_2 by fast growing plants; finally forming a carbon sequestering solid witch can be then mixed with soil with various effects on the plant growth **[9, 10]**.

b) Carbon Nanocomposites

Carbon nanocomposites display versatile allotropic morphologies, physical-chemical properties and a wide range of applications such as mechanical, electronics, structural material, chemical processing and energy management. Using hydrothermal carbonization in the presence of water soluble metal salts, or preformed nanoparticles we can obtain carbon/metal (oxide) nanocomposites in one step process **[11]**. 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 **[12]**, while Pt on carbon aerogels as successful catalysts for methane direct oxidation to methanol **[13]**. Furthermore, the carbon matrix can be removed from these nanocomposites by simple calcination. Incorporation of a titanium containing precursor into the HTC process produces a nanostructured C/TiO_2 composite with visible light photocatalytic properties. **[14]** Additionally $LiFePO_4$/C mesocrystals with hierarchical porosities with (**Fig. 3**) can be produced in one step reaction for successful used as cathode in Li Ion Batteries **[15]**.

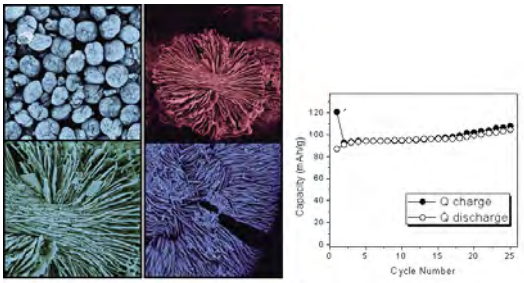

Fig.3: left: SEM micrographs of the $LiFePO_4$/C mesocrystals at various magnifications; right: charge/discharge capacity vs. cycle number plot for the $LiFePO_4$/C mesocrystals

c) Nitrogen Doped Carbon

The properties of carbon materials are dependent, to a large extent on the raw material, surface structure and porosity. However, the greatest effect on physicochemical properties of activated carbons is exerted by heteroatoms that are built into their structure (oxygen, nitrogen, boron, halogens, etc)

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.

The methods for the production of such materials relay normally on very harsh and multistep processes, which involve high temperature production of carbon materials followed by introduction of nitrogen to the structure using ammonia, amines or urea.

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 **[16]** or on hydrothermal carbonization of glucose in the presence of proteins **[17]**. The later approach leads to the production of carbon aerogels with high porosities, containing up to 9% nitrogen in their structures even at high post treated temperatures. This process and some SEM/TEM micrographs of such materials are shown in **Fig. 4**.

Another approach towards N doped porous carbons is simply taking see food waste products which contain high amounts of chitin as well as $CaCO_3$, followed by carbonization and removal of the inorganic using acetic acid. Thus the $CaCO_3$ can be used as a sacrificial template to obtain a high surface area material while the chitin is a suitable precursor for the production of N doped materials **[18]**.

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. Such materials have been applied already in important applications such as for example supercapacitors. Thus, the materials produced from glucosamine, followed by chemical activation turned out to be very promising candidates for electrodes in superacapacitors. This is due to the fact that besides the high surface area, they also contain up to 8 %N within their structure which leads to an increase in capacity (~ 300 F/g) related to some redox reaction with the electrolyte **[19]**. Furthermore the same N-doped materials also proved to have a significant uptake and selectivity for CO_2 versus N_2 **[20]** as well as a very high thermal and electrical conductivity **[21]**.

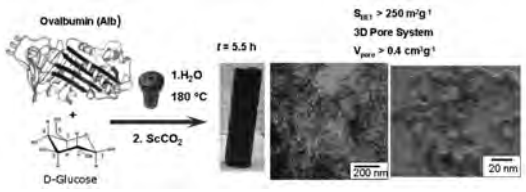

Fig. 4: Schematic process illustrating the production of nitrogen doped carbon aerogels from albumine and glucose together with two TEM micrographs illustrating their highly porous structure

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De Novo Nanoparticles: Novel Synthetic Routes for Nanoparticle Production

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1. Introduction

In 1857, Sir Michael Faraday prepared a sample of pure colloidal gold and described it for the first time in scientific terms. Faraday's work was inspired by the alchemist Paracelsus **[1]** and has driven generations of scientist toward nanomaterials. The remarkable properties exhibited by nanoscale materials are nowadays well-known and investigated mostly for metals and metal oxides, but just partially studied for other materials, such as metal nitrides (MN) and metal carbides (MC).

MN/MC nanostructures show potential in a diverse range of applications due to their unique properties. The most important placing them at the borderline between metals and ceramics, being e.g. conductive and active catalysts as pure metals but, at the same time, harder, longer lasting and resistant in harsh conditions. All these characteristics make them a valid and/or complementing alternative to pure elements or metal oxides.

Motivated by these appealing features, we set up a general, safe and competitive synthetic procedure to simplify and potentially scale up MN/MC production as nanostructures. Through complexation of metal complexes by urea molecules (or close derivatives), gels are formed which enable to use all shaping processes of classical sol-gel chemistry.

In this route, familiarly addressed as "the urea-glass-route" **[2]**, urea plays the double role of nitrogen/carbon source and stabilizing agent, and allows the production of a wide set of nanosized and highly crystalline metal carbides and nitrides with high specific surface area (up to 400 m^2/g) **[3]**.

As an example of their potentialities, as prepared iron carbide, molybdenum and tungsten carbides/nitrides nanoparticles have been tested as catalysts in ammonia decomposition process (a process for CO free hydrogen production, e.g. for fuel cell applications). The first promising results place these materials as a valid alternative to conventional catalysts (currently ruthenium based systems) **[4]**.

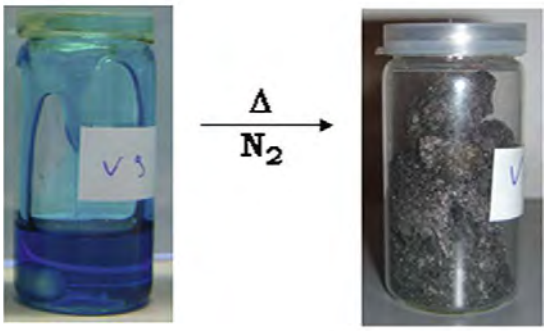

Fig.1: Vanadium-urea gel-like starting material (left side) and corresponding VN powder after heating treatment (right side).

2. Magnetic Nanostructures and Novel Ferrofluids

Seeking for alternative magnetic materials to iron oxide, we focused our attention to iron nitride and carbide, due to the higher stability against oxidation (compared to elemental iron), superior magnetic properties (compared to FeO_x) and an extreme hardness. In particular, Fe_3C can rank as an ideal candidate to extend Fe° and FeO_x in nanoapplications, say as an MRI contrasting agent or for the generation of stronger ferrofluids. Crystalline Fe_3C nanoparticles (d~ 7 nm) can be easily obtained by the soft urea pathway **[5]** and can be dispersed in water using a PEG based surfactant, generating a novel iron carbide based ferrofluid.

Simply by playing with external parameters such as iron precursors, C-source, use of hard template or additives, nanosized Fe_3C with different morphology (specifically nanoparticles and mesoporous material) have been obtained **[3, 4]**.

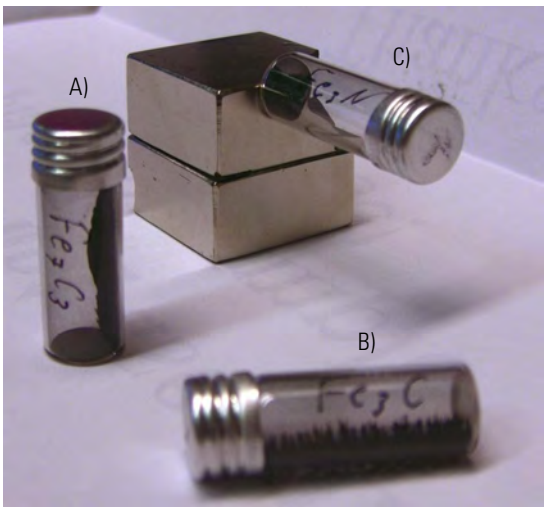

Fig. 2: Selection of as prepared magnetic materials: A) Fe_3C, B) Fe_7C_3 and C) Fe_3N.

3. Bio-Templating of Metal Carbides and Nitrides

In order to better control nucleation and growth of the intermediate ceramic phases, a biotemplating based route to metal carbides and nitrides has been developed. By dispersing aqueous metal salts within a biopolymer matrix, the nucleation of these intermediate precursors (often an oxide phase) is constrained to the nanoscale. On further heating, the carbon or nitrogen-rich decomposition products of the biopolymer react with these oxide nanoparticles, forming carbide **[6]**, or nitride nanoparticles.

Substituting single biomolecules with hierarchical biological template, we found out that the complex microstructure can be fully template. In particular, the complex structure of leaf veins with the magnetic material Fe_3C has been shaped. **[7]**

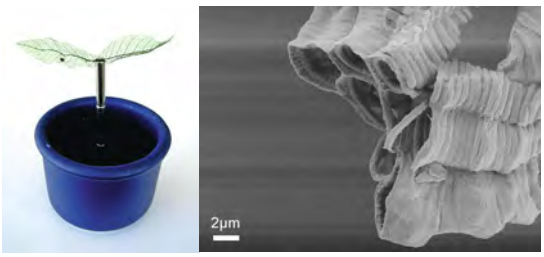

Fig. 3: Metaphoric picture (A) and SEM image (B) of the magnetic sacred fig (ficus religiosa) leaf replica, showing helical pitted structure characteristic of the replicated xylem vessels.

4. Advanced Nanofibres

Particulates are surely the simplest and easiest systems to handle in nanoscience, however non-spherical morphologies including anisotropic shapes such as nanofibres can bring additional features (e.g. anisotropic magnetism and optical properties). Electrospinning is a well-developed technique for fiber generation, from micro to nanometers. By combining the urea glass route **[2, 3]** with electrospinning techniques, it was possible to design various nanostructured fibers simply by structuration and calcination of the gel precursors. **[8]**

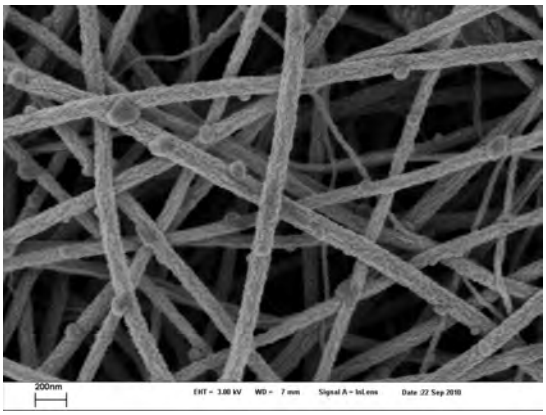

Fig.3: Fe_3N nanofibres prepared by polymer assisted urea glass route, at 600°C.

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Artificial Photosynthesis

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Thesis: Functionalized porous titania nanostructures as efficient photocatalysts
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(Dept. Chem.,The Chinese University of Hong Kong)
2006-2007: JSPS Research Fellow.
(Dept. Chem. Sys. Eng.,
The University of Tokyo)
2007-2009: Alexander von Humboldt Research Fellow
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Since 2005: Professor
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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 hydrocarbons and oxygen. 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 electronic, optical, and textural structures as potential energy transducers for artificial photosynthesis.

Synthesis of New g-C_3N_4 by Co-polymerization

We recently introduced graphitic carbon nitride (g-C_3N_4) as a metal-free photocatalyst **[1, 2]**. This offers new opportunities for solar energy applications, because covalent carbon nitrides are polymeric, cheap, abundant and stable materials with easily-controllable surface and bulk properties. Nevertheless, there are some drawbacks for this new photocatalyst, such as insufficient sunlight absorption (λ<460 nm) and low quantum efficiency. To solve these problems, a co-polymerization approach was developed to synthesize new carbon nitride structure, see **Fig. 1**. After co-polymerization with barbituric acid (BA), a remarkable red-shift of optical absorption from 470 to 750 nm and a 5 times higher activity of hydrogen production can be achieved. **[3]**

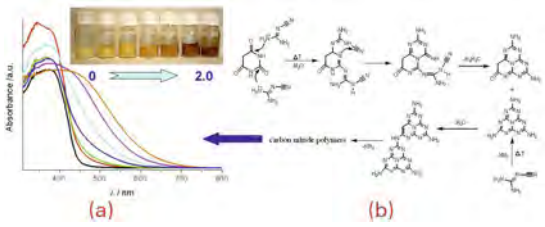

Fig. 1: Light absorption of new carbon nitride structure (a) and the proposed copolymerization processes of dicyandiamide with barbituric acid (b). Inset (a) is the picture of new carbon nitride samples

Synthesis of SBA-15-Type g-C_3N_4

To increase the photocatalytic activity of g-C_3N_4, nanosized pores have been created in bulk g-C_3N_4 to enlarge its external surface area **[4]**. Using mesoporous silica (SBA-15) as a hard template, a rod-like ordered mesoporous g-C_3N_4 (ompg-C_3N_4) was obtained, see **Fig. 2**. Ompg-C_3N_4 possesses a large surface area (239 $m^2.g^{-1}$), uniform pore size, and a 2D accessible framework. The hydrogen evolution rate of this nanoporous C_3N_4 was five times higher than that of bulk g-C_3N_4. **[5]**

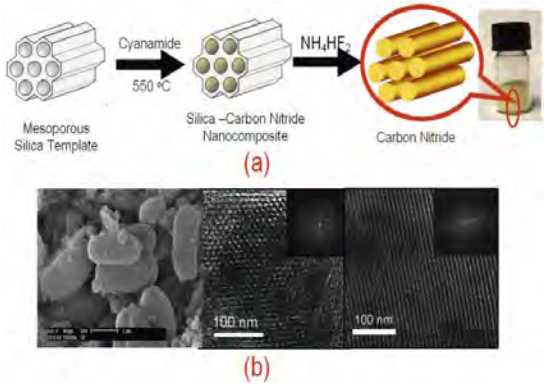

Fig. 2: Pathway for the synthesis of ompg-C_3N_4 (a) and its SEM and TEM characterizations (b).

Sulfur-Mediated Synthesis of g-C_3N_4

Classic C_3N_4 solids are prepared by the bulk condensation route using nitrogen-rich monomers (e.g., cyanamide, melamine, and melem) containing $–NH_2$ motifs as the leaving groups during the polycondensation. This bulk deamination reaction, however, suffers from incomplete polymerization due to kinetic problem. We have demonstrated that using amino-group-free trithiocyanuric acid as precursor where the –SH groups act as the leaving groups to synthesize carbon nitride (CNs) can offer an effective approach to modify its texture, optical and electronic band structure properties, as well as the photocatalytic activity, see **Fig. 3**. The water splitting reaction has been achieved at a moderate rate with bare C_3N_4 without using co-factors. **[6]**

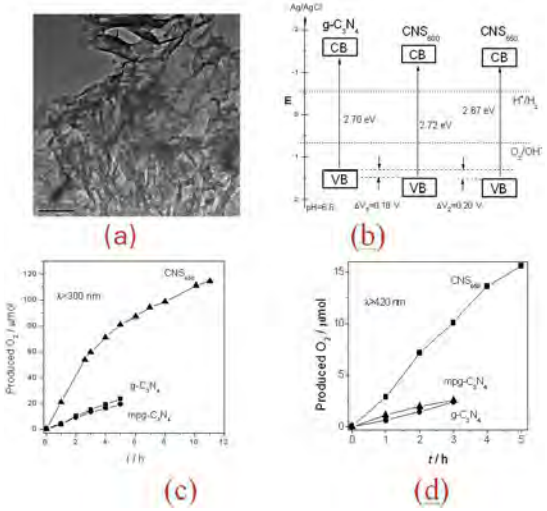

Fig. 3: A typical TEM image of C_3N_4 synthesized by a sulfur-mediated approach (a) and electronic band structure of classic g-C_3N_4, CNS_{600} and CNS_{650} (b). Oxygen-evolution by g-C_3N_4, mpg-C_3N_4 and CNS_{650} as a function of time under UV (c) and visible light illumination (d).

Heterogeneous Organophotocatalysis

We analyzed the electronic band structure of g-C_3N_4 by electrochemical methods. Results revealed that the conduction band (CB) and valence band (VB) of g-C_3N_4 are located at -1.3 V and +1.4 V vs. NHE, respectably **[3, 6]**. Light-excited electrons in the CB of g-C_3N_4 possess a large thermodynamic driving force to reduce O_2 ($E^0(O_2/\bullet O_2^-)$ = -0.16 V), but the potential of the photogenerated hole in the VB is inadequate to oxidize -OH to /•OH (E^0(-OH/•OH) = 2.4 V), see **Fig. 4a**. These features provide an argument that g•-C_3N_4 might act as a suitable candidate for photooxidation and related transformations. g-C_3N_4 was therefore chose as a organocatalyst for selective oxidation of alcohols **[7]** and oxidative coupling of amines **[8]** using molecular oxygen and visible light, see **Fig. 4**.

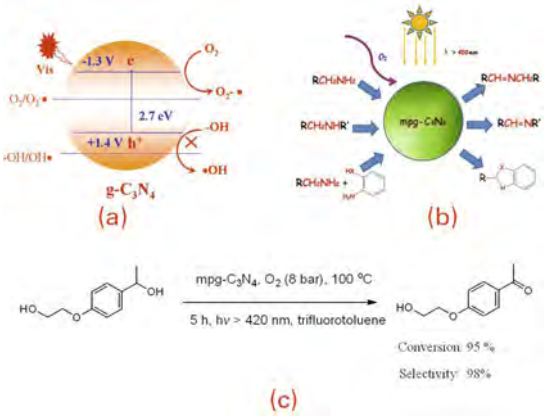

Fig. 4: Electronic band structure of g-C_3N_4 (a). Selective oxidation of alcohols (b) and oxidative coupling of amines (c) photocatalyzed by carbon nitride.

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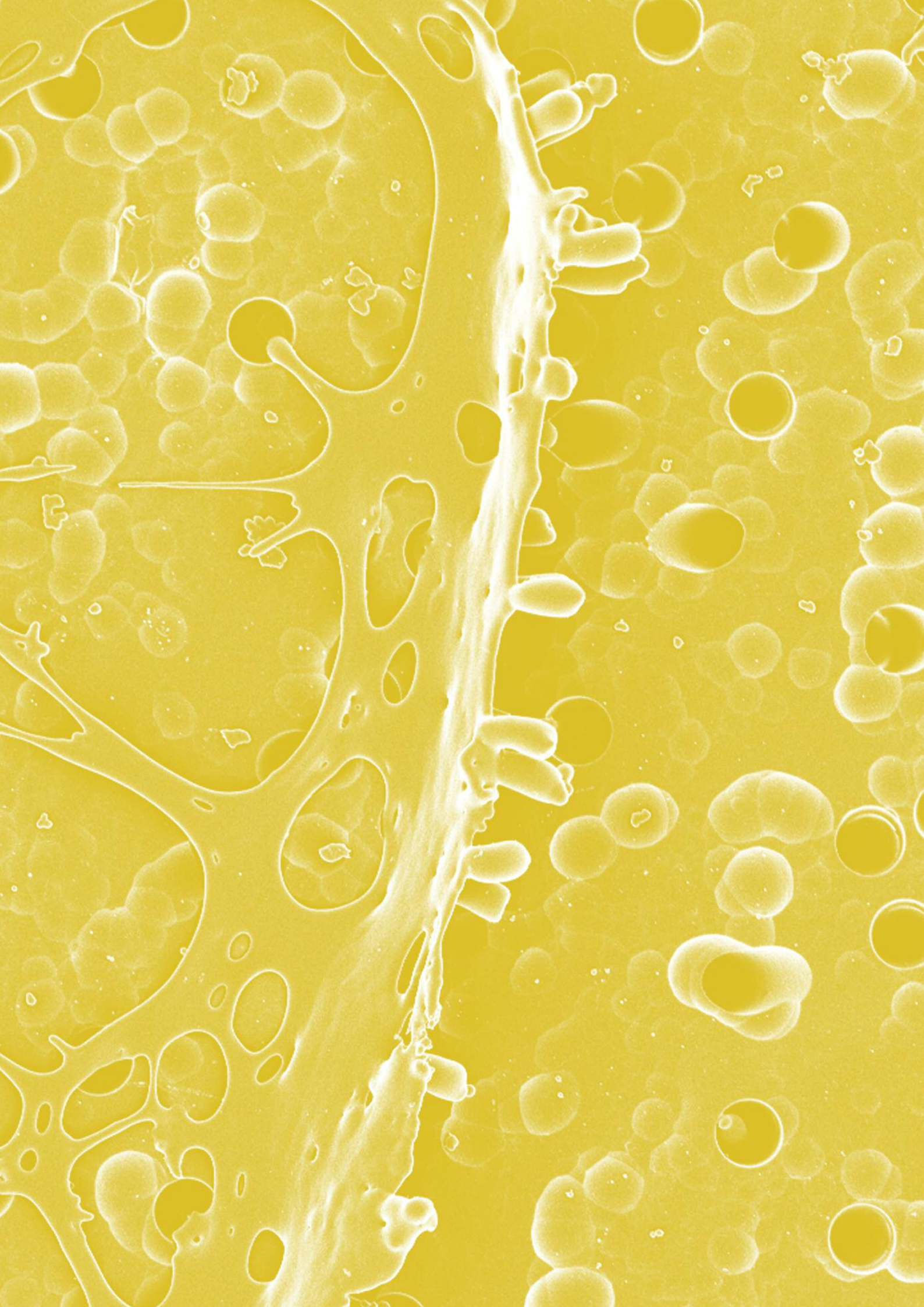

→ (Quasi) Planar Interfaces – Fluid Interfaces
→ Solid Interfaces
→ Non-Planar Interfaces
→ International Joint Laboratory
→ MPI-NIMS International Joint Laboratory

INTERFACES

Research in the Department of Interfaces

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

I. General Strategy

Interfaces are most important on one hand to understand and control colloidal systems with their large fraction of specific surface, on the other hand most processes start at an interface, and therefore they determine many physical and chemical properties. From a basic science point of view they exhibit peculiarities as low – dimensional systems and are anisotropic systems where molecules can be oriented. Within the institute's strategy of building and understanding hierarchical structures they are positioned at the lowest length scale which one may also consider the base. Accordingly the main aim of the department is to understand and to control molecular interfaces as regards structure, dynamics and properties. As an offspring of this the knowledge could be used to prepare complex films, coated colloids and capsules. For this the department has established a zoo of techniques to characterize colloids and interfaces and, especially concerning studies of liquid interfaces, we are probably best equipped world – wide. The latter is also due to the fact that there has been a continuous development of methods over years. Part of these developments has been commercialized within 4 start – up companies.

As a general trend in all groups the interfaces increase in complexity, i.e. planar interfaces mostly also contain proteins, polypeptides or nanoparticles. If the interface contains only small molecules the dynamics is of prime importance. One exception may be studies of ion binding to interfaces where the water structure is most important and where thus even simple charged molecules are good models.

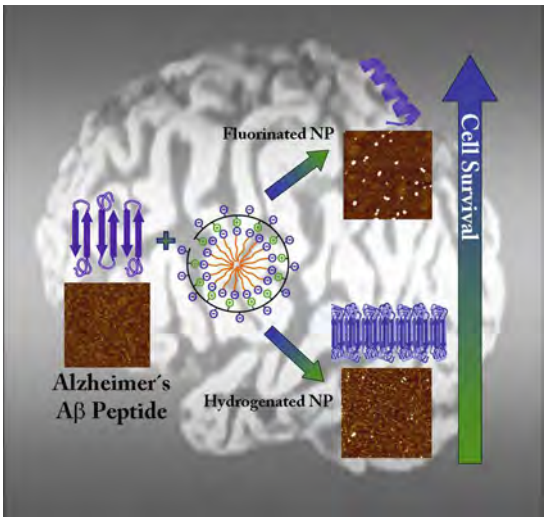
On the other hand the mission is also to concentrate on basic science and therefore schemes had to be developed to transfer technology and knowledge to groups and partners oriented towards application.

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

II. Research Highlights

II. 1 Planar Interfaces

The specially advanced expertise and methology to study Langmuir monolayers at the air/water interface has been made use of in many model studies of systems interesting for various type of applications, to name but a few:

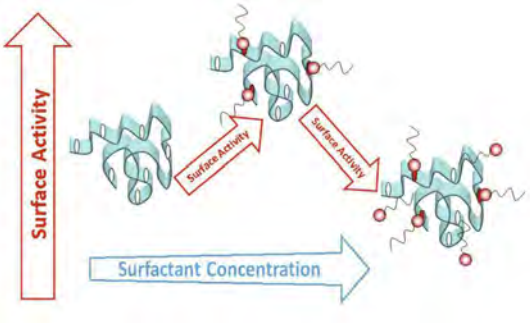


Dynamic fluorinated nanoparticles (NPs) induce α-helix-rich structures in Aβ peptides, prevent aggregation and increase viability of human neuroblastoma cells treated with Aβ oligomeric species, whereas their hydrogenated analogues lead to β-sheet formation and fibrillation.

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

The previous studies on enzymes

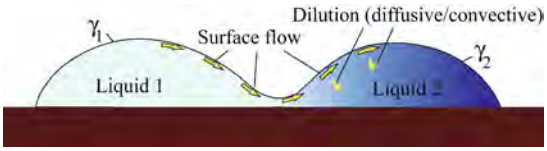
at interfaces have been interrupted due to a lack of cooperation partners and will be resumed now in cooperation with the department Biomolecular Systems.



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

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

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



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

II. 2 Non-Planar Interfaces

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

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

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

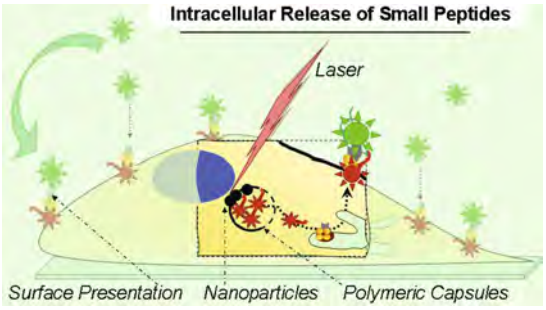
(B) Development of sonochemistry as a tool for surface and nanoparticle modification.

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

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

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

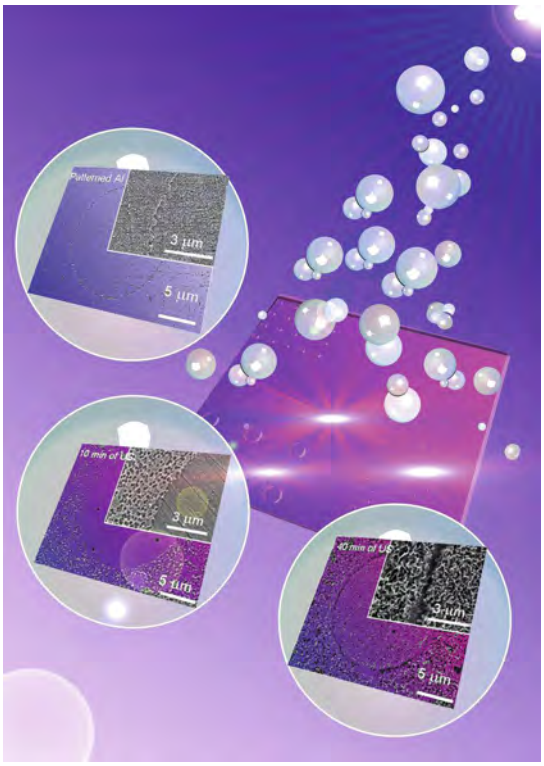
Another successful development of the group concerns multicompartment capsules and accomplishment of mechanically induced and directionally specific release.



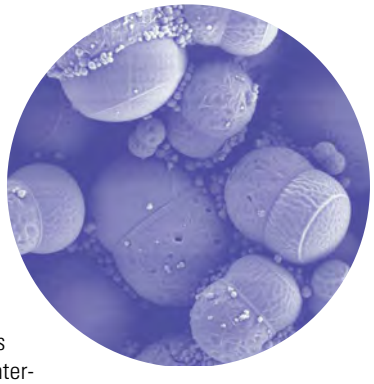
The group of *D. Wang* has had much success developing a simple method of fabricating Au nanoparticles of very uniform size and shape. It basically exists of modifying the well-established Turkevich method by adding trace amounts of silver nitrate. Thus nucleation of Au was facilitated and the multiple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

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

The joint German-French lab on sonochemistry has produced its first publications in the last 2 years. Sonoluminescence spectra could be obtained from single bubbles existing of broad emission of a continuum from which a plasma temperature could be derived and the narrow emission from atomic or radical species, both depending drastically on the acoustic pressure. In accordance with a derived nucleation and growth model it was shown with micropatterned surfaces that the process predominates on hydrophobic surface areas and the impact is due to a microjet resulting from bubble collapse.



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



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

III. Future Development

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

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

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

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

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

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

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

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

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

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

As mentioned before the department of interfaces will persist another 2-3 years, and it is a good tradition that a retiring director has no influence on the future direction and persons. It is also most desirable not to continue the "old" directions. Therefore I will not comment on any future perspectives of the department. On the other hand my colleagues are trying hard to maintain an institute with 5 departments and there is consensus that this should focus in a broad sense on physical chemistry. If they are successful this then would enable an easy transfer of scientific and technical staff into this department. On the other hand I am satisfied that up to now the shrinking process has not encountered many personal hardships, as technicians, PhD students and postdocs found attractive positions. Therefore those remaining do not feel to be on a sinking boat but on a ship with high speed, helping them to find proper directions. I hope this process can be continued in a harmonic way, because these people have very well served science, but above all science should serve people.

Helmuth Möhwald
Director of the Department of Interfaces

Langmuir Monolayers as Model Systems to Study Interactions at Interfaces

Gerald Brezesinski 02.04.1950
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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
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1982-1992: Research Scientist (Institute of Physical Chemistry, University of Halle/S.)
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Aims

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

Selected Achievements

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

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

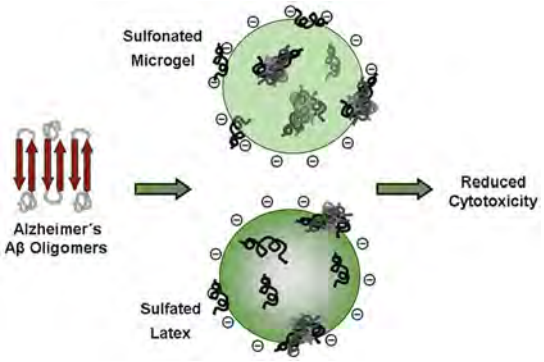

Fig. 1: Sulfonated and sulfated polystyrene NPs interact with Aβ peptide inducing randomization of its structure. As a consequence, the oligomerization process is disturbed and the peptide induced toxicity to neuroblastoma cells is reduced. These results comprise attractive achievements for the development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

Polymer Capped Fe_3O_4 Nanoparticles at the Air/Water Interface

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

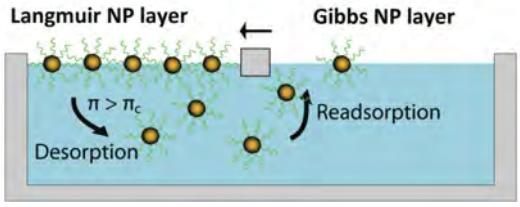

Fig. 2: Schematic representation of the desorption / re-adsorption of the Fe_3O_4@MEO_2MA_{90}-co-$OEGMA_{10}$ NPs from / at the air/water interface

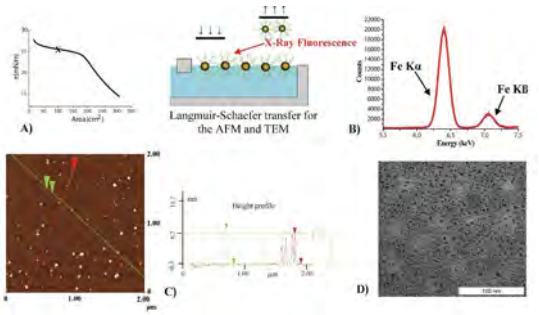

Fig. 3: A) Schematic representation of the NP layer at the air/water interface. The X mark on the compression isotherm (at 25 mN/m) shows the state where the film was investigated by TRXF, AFM and TEM; B) X-ray fluorescence showing the Fe Kα and Fe Kβ peaks C) AFM and D) TEM images of the NP Langmuir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

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

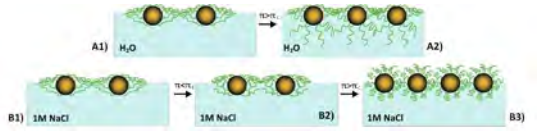

Fig. 4: Schematic representation of the interfacial behaviour of the Fe_3O_4@MEO_2MA NPs dictated by the conformational changes of the copolymer: A) below the LCST, the pancake-like configuration co-exists upon lateral compression with the brush conformation; B) above the LCST, the mushroom-like structure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

Future Plans

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

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

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

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

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

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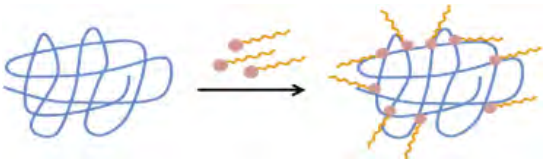
The main target of the group's activities comprises experimental and theoretical work on the thermodynamics and non-equilibrium properties of mixed protein-surfactant interfacial layers at water-air and water-oil interfaces. Work is under way to specify interfacial properties which correlate with the key parameters of corresponding foam and emulsion films, in particular their type, thickness and stability. The consequent question is whether the behaviour of foams and emulsions can be understood from the knowledge of the main properties of the corresponding adsorption layers and free films.

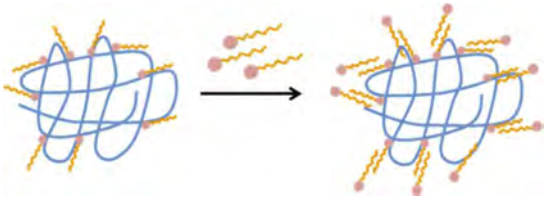
During the last five years we have been working intensively on various mixed protein-surfactant systems with the aim of understanding if and how adsorbed proteins can be replaced from the interface by surfactants, or prevented from adsorption by addition of surfactant to the solution, despite their much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

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



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

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



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

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

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

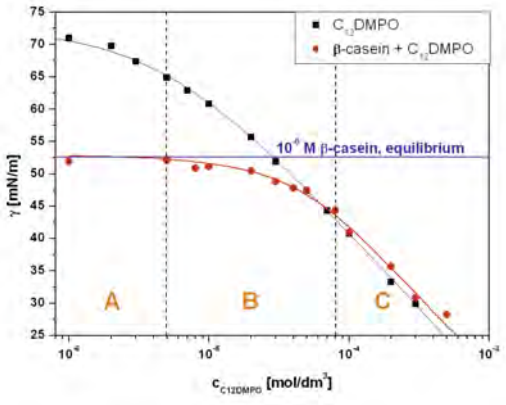


*Fig. 1. Adsorption isotherm of a mixed adsorption layer at a fixed amount of 10^{-6} mol/l β-casein and increasing concentrations of the non-ionic surfactant C_{12}DMPO, the red and black lines were calculated from the thermodynamic model for protein/surfactant mixtures and the surfactant alone, respectively;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

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

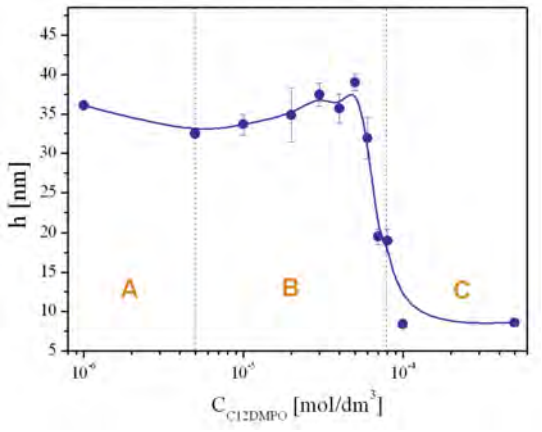


Fig. 2. Foam film layer thickness h of a mixed adsorption layer at a fixed amount of 10^{-6} mol/l β-casein and increasing concentrations of the non-ionic surfactant C_{12}DMPO; region A: mainly formed by the protein, region B: mixed layer; region C: transition to a pure surfactant layer; the curve is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

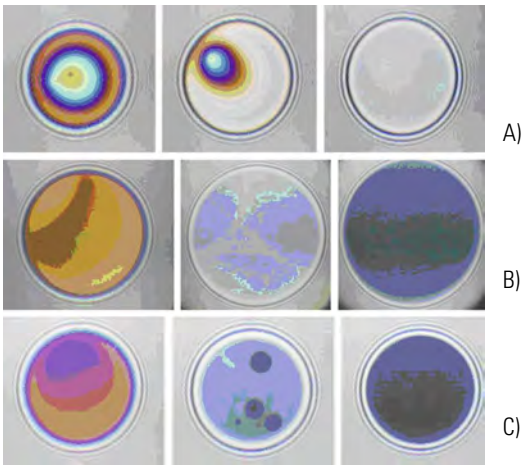


Fig. 3. Images of foam films corresponding to different states of the stabilizing mixed adsorption layers (the corresponding isotherm is given in Fig. 1 and film thickness given in Fig. 2) at a fixed amount of 10^{-6} mol/l β-casein;
A) 10^{-5} mol/l C_{12}DMPO; B) 8×10^{-5} mol/l C_{12}DMPO;
C) 5×10^{-4}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

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

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

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

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

R. Miller, V. Alahverdjieva, J. Bahtz G. Gochev, A. Javadi, Cs. Kotsmár, N.M. Kovalchuk J. Krägel, N. Moradi, N. Mucic, V. Pradines, A. Sharipova, S. Siegmund, V. Ulaganathan, D. Vollhardt, J.Y. Won, R. Wüstneck, (in close cooperation with E.V. Aksenenko, D. Exerowa, J.K. Ferri, V.B. Fainerman, V.I. Kovalchuk, M.E. Leser, E. Mileva and B.A. Noskov);
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Phase Transitions and Transport Phenomena in Thin Films at Solid/Air Interfaces

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

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

Work:

We investigate the following specific topics/questions:

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

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

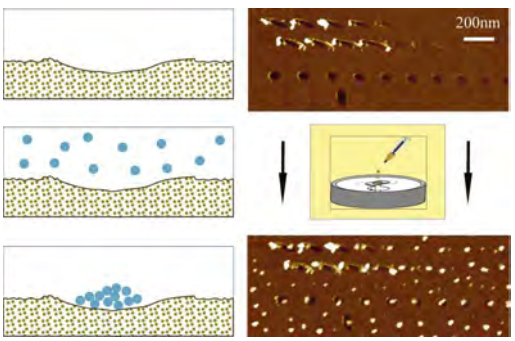

Fig. 1a: Influence of indentations in SiO_2 surfaces (depth <2nm!) on the location and growth of C60 aggregates.

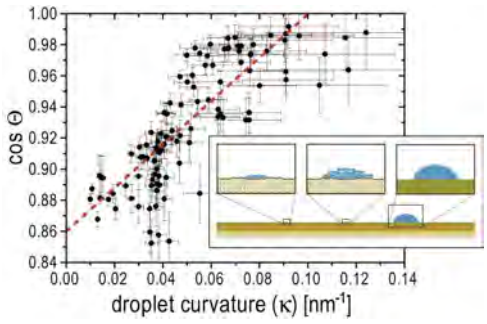

Fig. 1b: Contact angle as function of the curvature of the surface contact area (α inverse of droplet size) of C60 aggregates on SiO_2. The cartoon shows the variation of the aggregate shape with increasing volume.

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

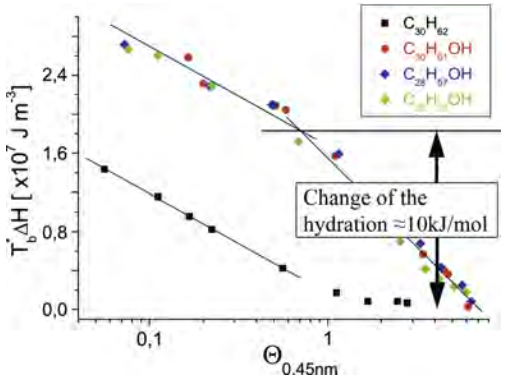

Fig. 2a: Lateral molecular interactions in alkane and alcohol submonolayers as function of the coverage. Below $1\Theta_{0.45nm}$ (= 0.45nm average coverage) both substances show the same 2-d gas behavior (identical slopes). Above, the alcohol interactions are dominated by changes in the hydration as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

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

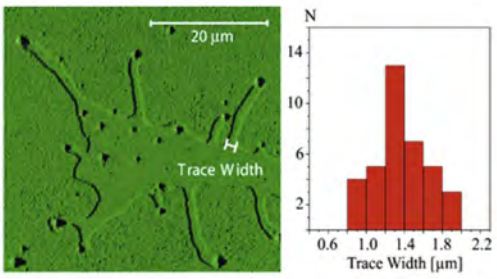

Fig. 3a: Surface partially covered with a solid alkane monolayer heated above melting and then rapidly cooled (→ fixed topology for AFM, trace width at the terrace edge = original droplet size).

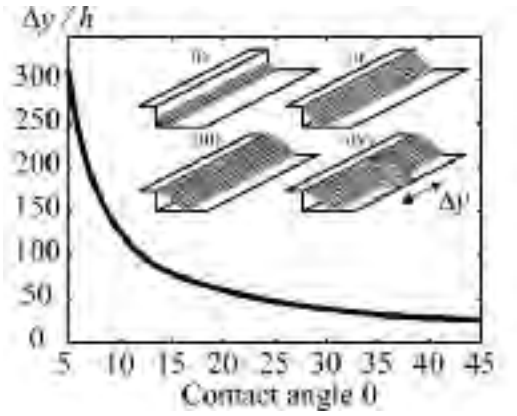

Fig. 3b: Channel morphologies at the terrace edge and bulge size $\Delta\gamma$ normalized to h as function of Θ.

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

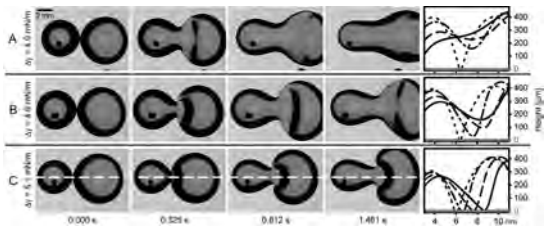

Fig. 4a: Time sequences of sessile drops on SiO_2 surfaces (top view). Rows A, B and C: various 1,2-butanediol/water mixtures (various $\Delta\gamma$) with fast (A) and delayed coalescence (B, C). Drop height profiles derived along the white line (C).

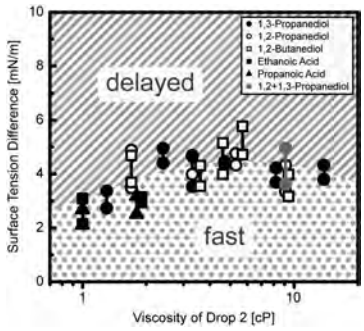

Fig. 4b: Phase diagram of the coalescence behavior: Surface tension difference $\Delta\gamma$ vs. viscosity ($\Theta \approx 10^0$). $\Delta\gamma$ >2-4mN/m leads to delayed coalescence.

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

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

Future Plans:

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

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Joint French-German Laboratory (LEA) on Sonochemistry

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Since 2006: Honorary Professor (Institute of Chemistry at the Chinese Academy of Sciences, Beijing)

General and Aims

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

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

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

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

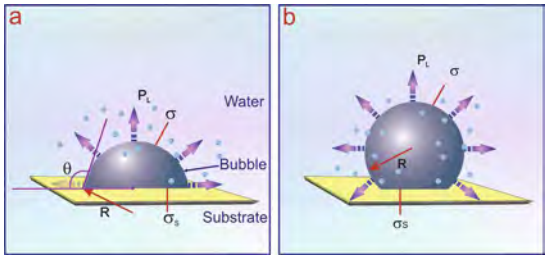

Fig. 1: Scheme of a bubble of radius R on a hydrophobic (a) and a hydrophilic (b) surface with solid surface energy σ_S liquid surface energy σ_L and contact angle Θ. The bubble grows because of a pressure difference P'- P_L between inside and outside.

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

Results

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

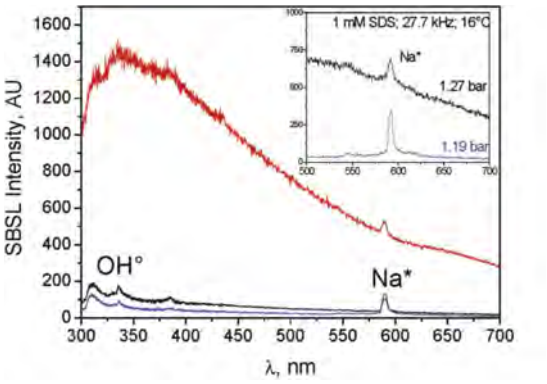

Fig. 2: Sonoluminescence spectra (28 kHz) of a 0.5M NaCl solution regassed with 70mbar Ar at acoustic pressures of 1.25 (red), 1.20 (black) and 1.15 (blue) bar. The inset shows the spectra after addition of 1mM SDS at two different acoustic pressures (indicated) [2]

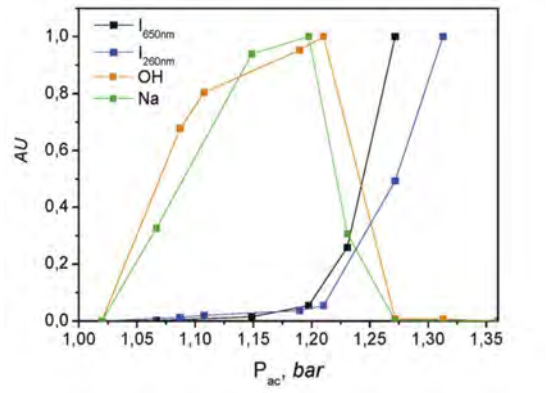

Fig. 3: Dependence of the sonoluminescence intensity on acoustic pressure P_{ac} for wavelengths corresponding to the broad emission (650nm, 260 nm) and for the lines ascribed to Ar and Na. [2]

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

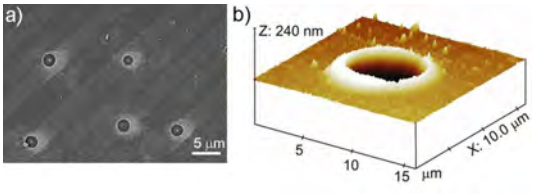

Fig. 4: (a) SEM image of a 100nm Al film on a micropatterned silicon wafer with the hydrophobic areas more bright after 10 min of ultrasonic treatment (20 kHz, 51.3 W/cm^2). b) AFM image of one of the spots on the left.

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

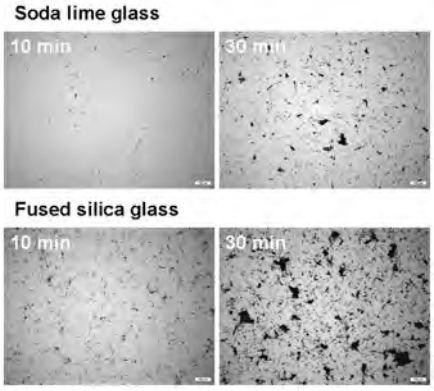

Fig. 5: Optical micrographs of two different glasses after 10' and after 30' ultrasonic treatment. [4]

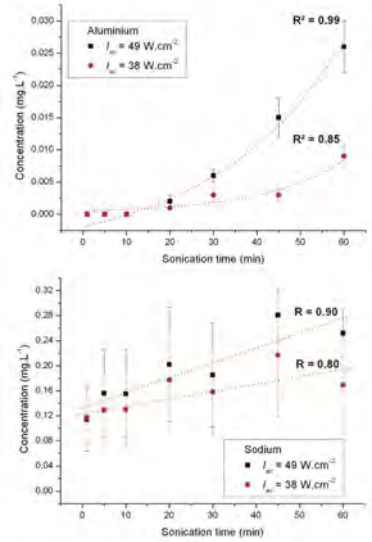

Fig. 6: Ionic concentration of Al (top) and Na (bottom) in solution as a function of sonication time for different intensities (indicated) [4]

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

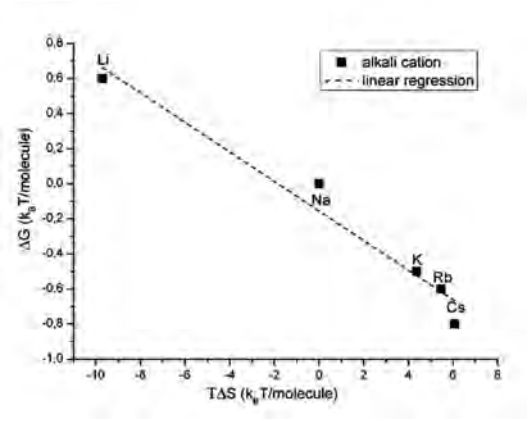

Fig. 7: Free energies of binding versus solvation entropy for different ions with Na^+ as reference [5].

Future Development

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

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

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

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Active Interfaces and Coatings

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Development of multifunctional coatings, which will possess active and rapid feedback activity in response to changes in local environment, is a key technology for fabrication of future high-tech products and functional surfaces **[1-7]**. These new multifunctional coatings should combine passive components of "classical" coatings and active components, which provide fast response of the coating properties to changes occurring either in the passive matrix of multifunctional coatings (e.g., cracks, local pH change) or in the local environment surrounding the coating (humidity, electromagnetic irradiation). The coatings could also have several functionalities.

The release properties and re-loading ability of polyelectrolyte-modified halloysite nanotubes, TiO_2 nanoparticles, and polyelectrolyte capsules were studied **[1-3, 5-7]**. All nanocontainers revealed an increase of the inhibitor (methylbenzothiazole, benzotriazole) release in aqueous solution at alkaline or acidic pH. The application of appropriate nanocontainers depends on the demands required from feedback active anticorrosion coatings. A novel approach of local corrosion termination using UV-irradiation has been studied. The possibility of release of corrosion inhibitor and fluorescent dye from titania based polyelectrolyte containers under UV-irradiation was demonstrated. Use the porous containers allows loading the wide spectrum of chemicals inside the containers, thus this system consists of nanosized reservoirs. A polyelectrolyte shell, which modified the outer surface of the containers prevents the untimely release of the loaded material. Moreover, nanocontainers with titania core revealed an increase of the benzotriazole (corrosion inhibitor) release under UV-irradiation twice faster in comparison with pH stimulated release. Simultaneously, the highest release efficiency under pH change in the corrosion process was up to 65%, for titania-based mesoporous nanocontainers, however, if one uses the UV-irradiation the release could be increased up to 86%. Thus it should be noted that for the coatings where very fast and regulated release is necessary, the use of UV-irradiation is strongly preferable.

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

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

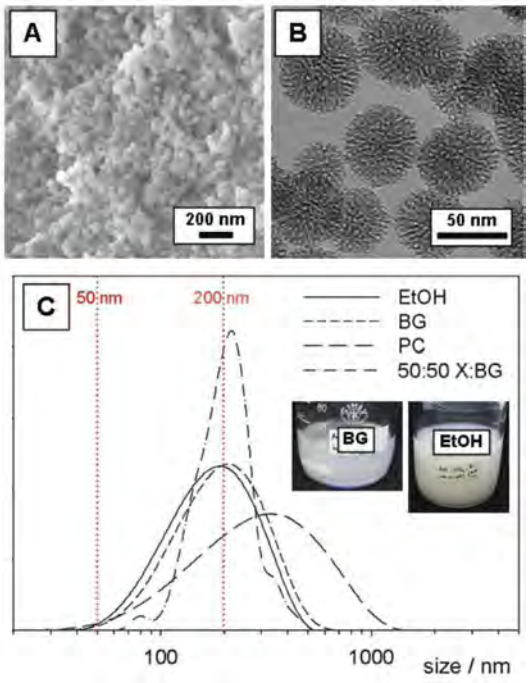

Fig. 1: A and B: SEM and TEM images of mesoporous silica nanoparticles (NPs). C: DLS profiles, and (inset) visual appearance of the NPs in different solvents of intermediate polarity. Key: EtOH = ethanol, BG = butyl glycol, PC = 1,2 propylene carbonate, X = xylene.

The collapse of the critical cavitation microbubble in liquids under ultrasonic treatment results in an enormous concentration of energy from the conversion of the surface energy and kinetic energy of the liquid motion into heat or chemical energy. The high local temperatures (5000-7000 K inside a cavitation bubble) and pressures combined with rapid cooling pro-

vide unique means for forming nanomaterials with non-equilibrium structure under extreme conditions **[8-14]**. The characteristics of the ultrasonically produced nanomaterials can be changed by decorating it with suitable hydrophilic and hydrophobic organic moieties.

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

Stable monodisperse gold, silver, and gold-silver alloy nanoparticles with the variable average diameter of 5-30 nm were used for modification by ultrasound at room temperature **[9, 10,]**. The prepared gold nanoparticles were mixed with silver salt or silver nanoparticles and successively sonicated step by step. The successive ultrasonic treatment was found as the optimal one because it helps to avoid undesirable aggregation of gold nanoparticles and partly reduces silver ions during the sonication. The type of surfactant influences the size and shape of gold-silver alloys as well as the duration of the ultrasonic treatment adjusts the complete reduction of silver ions on the gold surface. More than 1 hour of ultrasonic irradiation is required to create gold-silver structures with shape and depending on surface active additive XRD and ED patterns of final samples proved the presence of polycrystalline or amorphous gold-silver nanoalloys or gold nanoparticles.

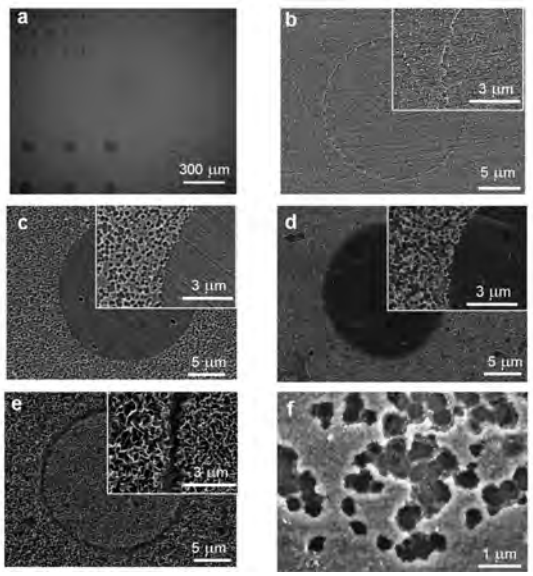

Fig. 2: SEM images of the patterned Al plate before ultrasonic treatment (a, b) and after ultrasonic treatment: (c) - at 10 min of sonication, (d) – at 30 min of sonication, (e) – at 40 min of sonication, (f) – high magnification of the hydrophobic surface with pits at 30 min of sonication. The inner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

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

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Ordering of Functional Nanoparticles

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

A. NP Synthesis

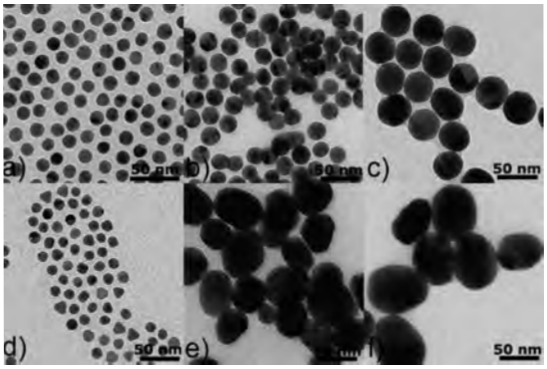

Fig. 1: TEM images of Au NPs obtained by the present method (a-c) and by the Turkevich method (d-f) at different citrate concentrations: 2.97×10^{-2} wt% (a,d), 1.01×10^{-2} wt % (b,e), and 6.10×10^{-3} wt% (c,f). The concentration of Ag+ ions in the present method was 8.5×10^{-6} wt%. The concentration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

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

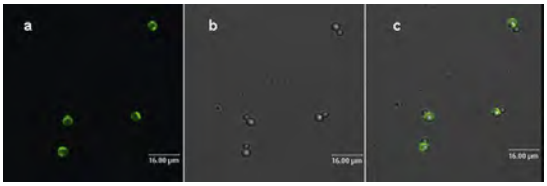

Fig.2: Fluorescence (a) and transmission (b) CLSM images of the anisotropic particles obtained by incubation of (PAH/PSS)3/FITC-PAH/PSS/PAH/PSS-coated 4.4 m PS particles in a THF/water mixture for 2 min, followed by redispersion in water with the means of centrifugation. (c) Overlay of the fluorescence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

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

B. Interfacial Translocation of NPs

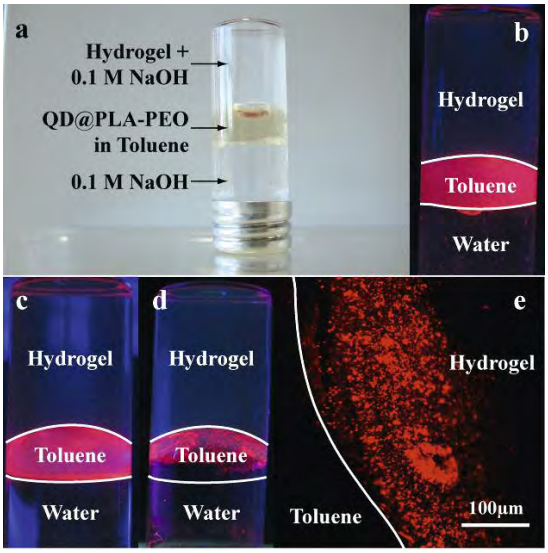

Fig. 3: CdSe@PLA/PEG NPs transfer from the organic phase to the aqueous phase in a triphasic system containing a NP toluene dispersion (the middle phase), a 0.1 M NaOH aqueous solution (the lower phase) and a hydrogel swollen by 0.1 M NaOH aqueous solution (the upper phase). The triphasic system was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

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

C. Shape-Controlled Self-Assembly of NPs

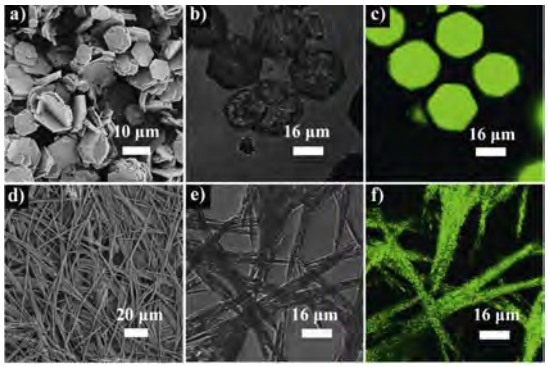

Fig.4 SEM (a and d) and CLSM transmission (b and e) and fluorescence (c and f) images of hexagonal flakes (a–c) and wires (d-f) obtained via controlled isotropic and anisotropic self-assembly of CdTe NPs stabilized by L-cystein.

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

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Nanotechnology and Optical Manipulations of Capsules and Films

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

The main goals of the group are:

- to understand intracellular transport of proteins and small peptides;
- to develop next generation of drug delivery vehicles for studying enzymatic reactions in models systems and in cells;
- to advance in the area of nano-manipulations;
- to investigate thermal properties of polymers and localized permeability control of membranes, films, polymers, etc.;
- to develop novel materials and membranes with built-in opto-electronic properties.

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

Using polymeric capsules and remote release methods, we have recently introduced remote and non-invasive methods of release of encapsulated materials inside living cells. **Fig. 1** demonstrates intracellular release of SIINFEKL peptide inside a cell containing MHC (major histocompatibility complex) Class I molecules. The walls of the capsule are functionalized nanoparticle aggregates which absorb light energy and convert it to heat. These nanoparticle aggregates produce absorption in the "bio-friendly" near-IR (infrared) part of the spectrum. The aggregation of nanoparticles can be induced either by concentration or by shielding the stabilizers on the nanoparticles. Local, nanometer-size, heating by a near-IR laser light affects the permeability of the outer polymeric shell allowing materials to be released remotely. Intracellularly released peptides allow investigation of transport and cell surface presentation of proteins inside living cells – this area of research is of fundamental importance to immunology.

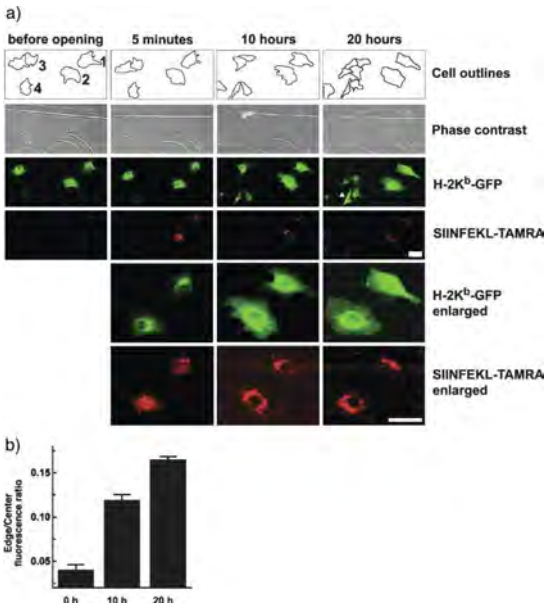

Fig. 1: Release of fluorescently labeled SIINFEKL peptide from the microcapsules leads to surface transport of H-2Kb–GFP without harmful side effects to the cells. a) Time course of capsule opening and class I transport. In cells 1 and 2 only, the microcapsules were opened at 0 min, and the TAMRA fluorescence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

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

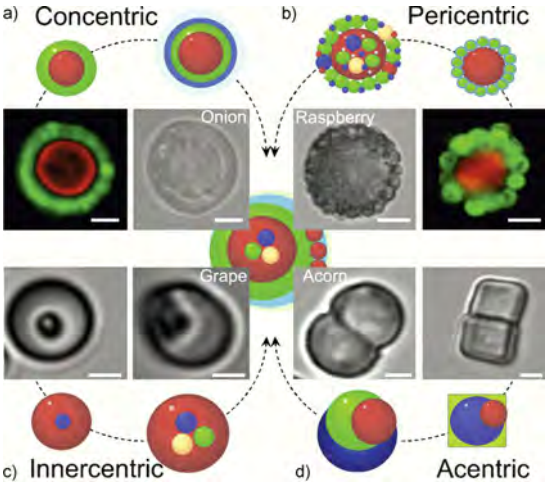

Fig. 2: Overview and the road-map for future directions of multicompartment microcapsules. Four different approaches are identified in the schematics: a) concentric, b) pericentric, c) innercentric, and d) acentric. The structure in the middle incorporates all four approaches. The corresponding confocal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

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

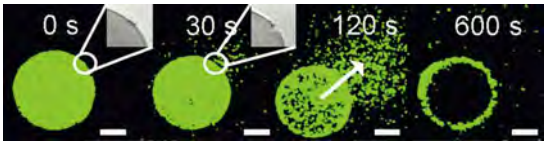

Fig. 3: Fluorescence microscopy snapshots of the site-specific opening of a giant polyelectrolyte capsule by IR laser activation. The inset shows the pore in the polyelectrolyte shell. The arrow indicates the direction of release as osmotic pressure drives encapsulated material out of the capsule.

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

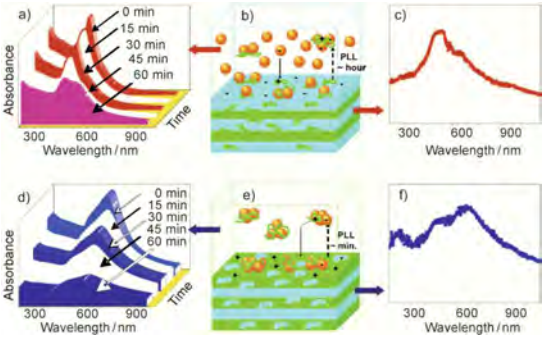

Fig. 4: Kinetics of adsorption of non-aggregated (a–c) and aggregated (d–f) nanoparticles onto biocompatible PLL/HA films. [Adsorption on (PLL/HA)24 films is shown in (a–c), while adsorption on (PLL/HA)24PLL films is demonstrated in (d–f)]. UV/Vis absorption spectra of the supernatant solution during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

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

Future Tasks:

- Investigation of intracellular transport properties relevant to immunology [with Jacobs University Bremen]
- Understanding mechanical properties of drug delivery vehicles for designed enhanced carriers and use them as intracellular sensors [with Bayreuth University, Bayreuth]
- Studying thermal properties of ultrathin membranes on the nanoscale
- Nanoparticle self-assembly at the polymer-water interface for remotely activatable, biocompatible planar thin films/particles and for renewable energy applications
- Bio-compatible films [with Fraunhofer Institute of Biomedical Technology, Golm]
- Novel materials with optical and opto-electronic properties.

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Molecular Assemblies of Biomimetic Systems and Nanostructured Design

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

Self-Assembly of Dipeptide Nanostructures

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

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

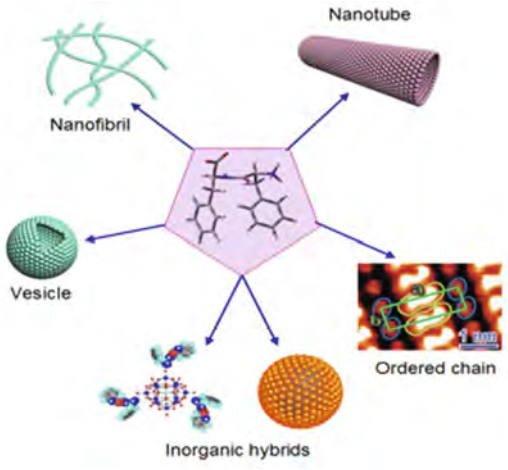

Fig. 1. Schematic representation of various nanostructures formed by self-assembly of FF-based building blocks.

Transportation of Assembled Capsules Driven by Motor Proteins

The linear molecular motor, kinesin, transports chemical payloads along microtubules in the cell. The used growing filament, a microtubule, is polar and has two functions: provide rails or tracks for the kinesin motors and limit the movement into a certain direction. Our group currently focuses on the design and assembly of active biomimetic systems which involve the surface modification of microcapsules with well defined properties, purification of microtubules to link the biomolecular motors, stepping motor proteins, kinesin and the complete assembly of the system. We try to provide experimental evidence how the molecular motors generate pull forces to drive hollow capsule transportation along the microtubules and further understand the force generation mechanisms. The final system aims at a specific function of hollow capsules as a useful "cargo" for drug delivery in a living matrix by making use of molecular motors. For instance, we recently fabricated an active biomimetic system based on the microcapsule-kinesin motor-microtubule complex. In this active biomimetic system, the microtubules act as shuttles that transport the attached polymer microcarriers. We found that the velocity of the movement does not depend on the size of the capsules but the fraction of mobile capsules depends on capsule size and biotinylation proportion of microtubule. The microtubule could also propel dextran-filled capsules to transport the internal components on the activated surface. The study integrates artificial materials into the kinesin-microtubule system and provides a potential use for straightforward and facile transport of polymer materials and fabrication of hybrid microdevices for biochemical sensing and delivery applications (**Fig. 2**).

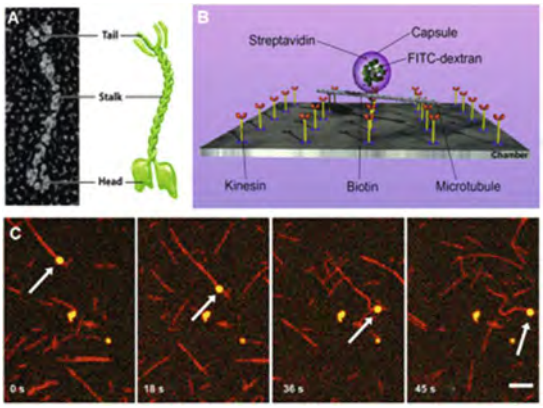

Fig. 2. layer-by-layer assembled capsule as a cargo pulled by a microtubule along the kinesin-modified channel. (A) Structure of kinesin motor protein; (B) Transport of a polymer microcapsule filled with dextran by a microtubule on a kinesin-coated surface. The capsule is coated by streptavidins, thus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

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Supramolecular Architectures

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Although typical (hydrophilic/hydrophobic) amphiphiles such as surfactants and lipids are well matured and the formation mechanism of their nano/microscopic structures is well understood, our uncommon hydrophobic amphiphiles (π-moiety and hydrophobic alkyl tails) have more possibilities to create versatile assembled architectures and function because of their dependence on the specific organic solvent. Therefore a delicate balance of the intermolecular interactions, such as van der Waals, π-π, hydrogen-bonding, leads to a wide variety of supramolecular morphology and this understanding of the hierarchical assembled systems should inspire further studies for supramolecular chemistry, biomimetic structures, nanotechnology as well as their materialization.

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

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

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

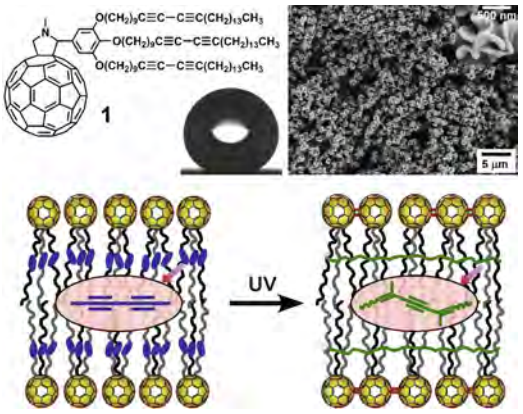

Fig. 2: A cartoon representation of the photo-cross-linking process in the bilayer structural subunit of 1. SEM image of flakelike microparticle assemblies of 1 and a photograph of a water droplet on the surface, contact angle ~ 150°.

A sustainable method for the fabrication of metallic surfaces with rose flowerlike fractal morphology was developed by using the supramolecular microparticles of **2**, possess on a nanoflake structure at the outer surface, as template (**Fig. 3**). Modifying Au nanoflakes with self-assembled thiol monolayers or polymers allows the surface wettability to be adjusted between superhydrophilic and superhydrophobic. Furthermore, Au nanoflakes present excellent substrates for surface-enhanced Raman spectroscopy (SERS). The enhancement factor is around 10^5 **[7]**.

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

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

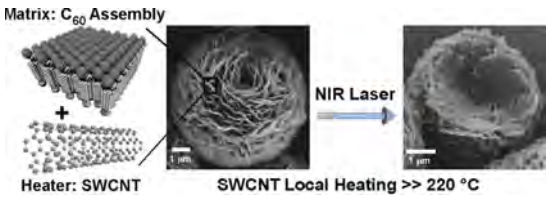

Fig. 4: Scheme of a temperature indicator for NIR photothermal conversion (>> 220 °C) of SWCNT in an assembly of 2 with flakelike microparticle structure.

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

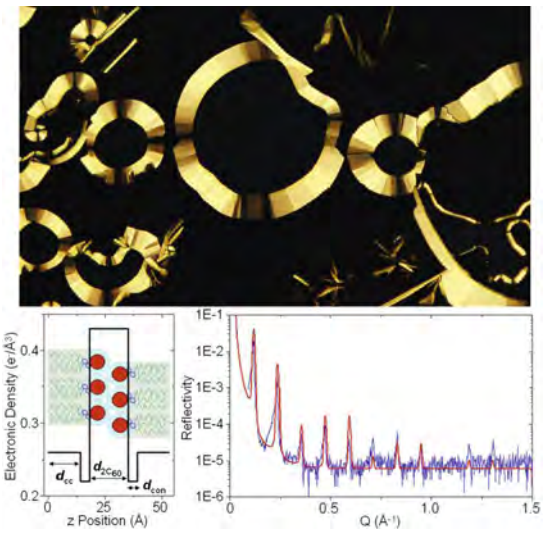

*Fig. 5: Texture of mesophase of **2** under POM. Three-box electronic density profile and comparison between corresponding model (red line) and experimental (blue line) XRD patter for **2** in the mesophase*

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

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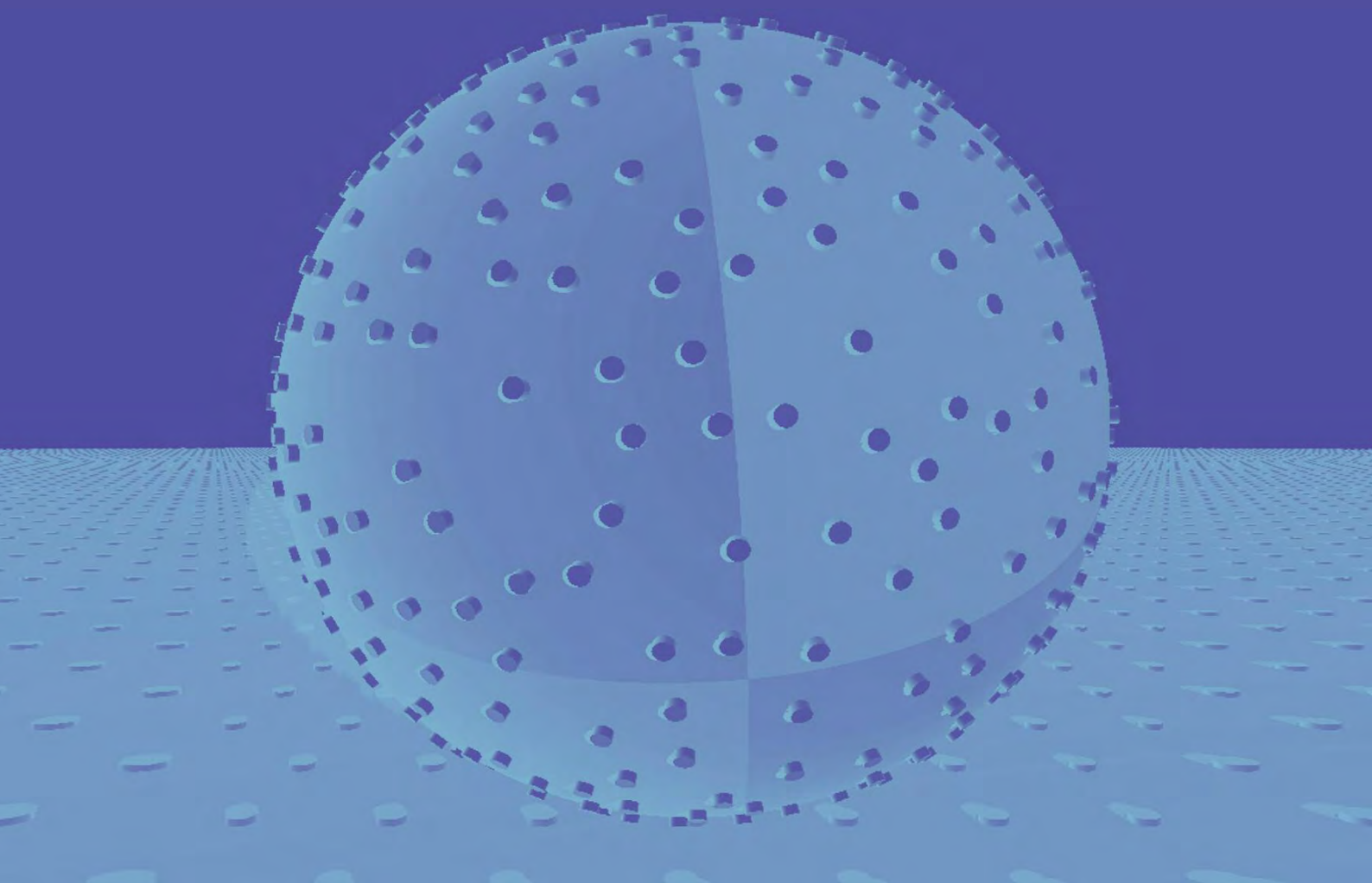
[11] Babu, S. S., Saeki, A., Seki, S.,Möhwald, H., Nakanishi, T.: Millimeter-sized flat crystalline sheet architectures of fullerene assemblies with anisotropic photoconductivity. Chem. Phys. **13**, 4830-4834 (2011).

→ Polymers and Proteins
→ Carbohydrates
→ Membranes and Vesicles
→ Complex Systems

THEORY & BIO-SYSTEMS



Research in the Department of Theory & Bio-Systems

Das Leben besteht in der Bewegung.
Aristoteles

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1978: Diploma, Physics, (University of Heidelberg)
1982: PhD (Dr. rer. nat.), Physics (University of Munich)
1979-1984: Teaching Associate (University of Munich)
1984-1986: Research Associate (Cornell University)
1986-1988: Group leader (FZ Jülich)
1987: Habilitation, Theoretical Physics (University of Munich)
Thesis: Critical behavior of interfaces: Wetting, surface melting and related phenomena
1989-1990: Associate Professorship (University of Munich)
1990-1993: Full Professorship (University of Cologne), Director of the Division "Theory II" (FZ Jülich)
Since Nov 1993: Director (Max Planck Institute of Colloids and Interfaces, Potsdam)

The main objective of our research activities is to understand the hidden dimensions of self-organization in biomimetic and biological systems. The molecular building blocks of these systems join "by themselves" and form a variety of supermolecular assemblies, which then interact to produce even larger structures and networks. Since these processes are difficult to observe experimentally on the relevant length and time scales, theory and computer simulations are essential in order to integrate different experimental results into a coherent and unified framework. The department is also responsible for the International Max Planck Research School on "Biomimetic Systems".

The associates of the department form several research groups. At present, the research group leaders and topics are:

· *Rumiana Dimova:* Biophysics Lab;
· *Volker Knecht:* Molecular Dynamics;
· *Thomas Weikl:* Proteins and Membranes;
· *Mark Santer:* Carbohydrates and Polysaccharides;
· *Christian Seidel:* Polymers and Polyelectrolytes;
· *Angelo Valleriani:* Stochastic Processes;
· *Stefan Klumpp:* Regulation of Bioprocesses.

The main results of these research groups are described in separate reports on the following pages. These reports are related to four main topics: Polymers and proteins, carbohydrates, membranes and vesicles, as well as complex systems. Both carbohydrates and complex systems represent relatively new research fields in the department.

As far as membranes and vesicles are concerned, two particularly interesting results are about the cooperative binding of membrane-anchored receptors, see **Fig. 1** and separate report by *T. Weikl*, and the formation of membrane nanotubes induced by aqueous phase separation, see **Fig. 2** and my separate report.

Other topics that are only partially covered in the subsequent reports include the multiscale motility of molecular motors and the dynamics of filaments. In the following, I will briefly summarize our recent results on these topics.

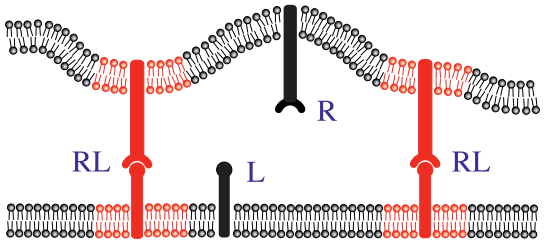

Figure 1: Cooperative binding of membrane-anchored receptors (R) and ligands (L). Binding requires that R and L are located opposite to each other and that the separation of the corresponding membrane segments matches the length of the RL-complexes.

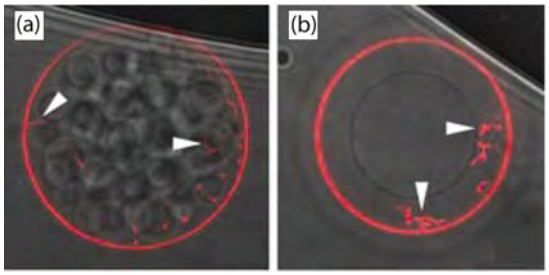

Figure 2: Membrane nanotubes within a lipid vesicle as indicated by the white arrows (a) during and (b) after aqueous phase separation within the vesicle. The fluorescently labeled membrane (red) forms both the large vesicle (outer circle), which has a diameter of about 40 µm, and the thin nanotubes, which have a thickness below optical resolution.

Motility of Molecular Motors.
We have focused on a particular class of molecular motors, namely motors that step along cytoskeletal filaments. Such stepping motors are essential for intracellular transport within eukaryotic cells as well as for their locomotion and division. All stepping motors have a similar molecular architecture with two identical motor domains, both of which are able to hydrolyze ATP into ADP and inorganic phosphate (Pi) as well as to dock onto the cytoskeletal filaments. In the last couple of years, we studied the multiscale motility of these motors on three different levels: conformational changes of motor proteins; free energy transduction by single motors; and cargo transport by motor teams.

Conformational Changes of Motor Proteins.
When viewed with atomistic resolution, each motor domain of kinesin contains several subdomains: the nucleotide binding pocket, the microtubule binding site, and the neck linker, see **Fig. 3**. After ATP has been bound to the empty nucleotide binding pocket, it is hydrolyzed into ADP and Pi, both of which are successively released from the pocket. We have studied the associated conformational changes by atomistic Molecular Dynamics simulations, which revealed a certain allosteric coupling between the different subdomains (*A. Krukau, V. Knecht*).

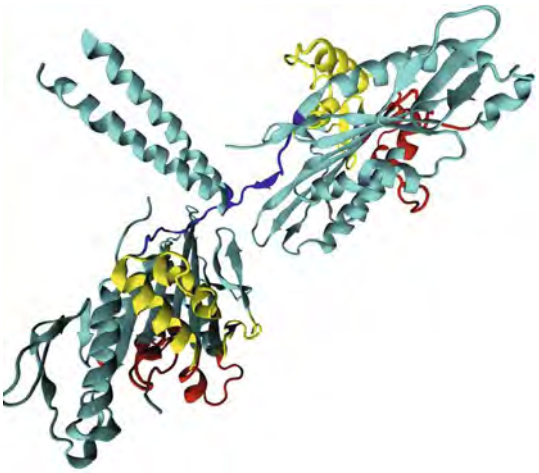

Figure 3: Two motor domains of kinesin (ribbon representation). Each motor domain contains a nucleotide binding pocket (red), a microtubule binding site (yellow), and a neck linker (blue). The „crosstalk" between these different subdomains depends on the occupancy of the nucleotide binding pocket (empty, ATP, or ADP).

Free Energy Transduction by Single Motors.
Since each motor domain can exhibit three different nucleotide states, a dimeric motor with two such domains can attain nine such states. These states are connected by chemical and mechanical transitions and form a chemomechanical network with a large number of motor cycles. Such a representation has been used to integrate many experimental data for two different stepping motors, namely for kinesin in contact with microtubules (*S. Liepelt, A. Valleriani*) and for myosin V that walks along actin filaments (*V. Bierbaum*). Both kinesin and myosin V are characterized by a competition between several motor cycles.

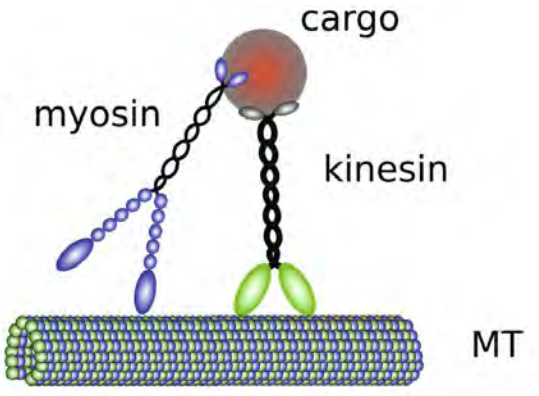

Figure 4: Cargo transport by the microtubule-based motor kinesin is enhanced by the actin-based motor myosin V. The latter motor binds to microtubules (MT) as well and then diffuses along these filaments. Vice versa, kinesin can bind to and diffuse along actin filaments. In this way, the two types of motors can transport the same cargo along both microtubules and actin filaments.

Cargo Transport by Motor Teams.
The transport of cargo within eukaryotic cells is performed by teams of molecular motors. Because each motor unbinds from the filament after a certain number of steps, the number of actively pulling motors varies with time. The case of two kinesins has been theoretically studied using two different representations of their state space (*C. Keller, F. Berger, S. Klumpp, S. Liepelt*). In some cases, cargo transport by one team of motors is enhanced by another team of motors that do not move in a directed manner but only diffuse along the filaments. One example is kinesin-driven cargo transport along microtubules that can be enhanced by the actin-based motor myosin V, see **Fig. 4** (*F. Berger, M.J.I. Müller*).

Depolymerization of Actin Filaments.
As mentioned, actin filaments provide the tracks for molecular motors such as myosin V. In addition, the polymerization and depolymerization of these filaments plays an essential role for many cellular processes such as cell division, locomotion, and adhesion. Quite recently, the depolymerization of single filaments was observed to be interrupted for extended periods of time. The interruptions are not coupled to ATP hydrolysis but arise from random modifications of actin protomers (*T. Niedermayer*).

For additional information about research at the Department of Theory & Bio-Systems, see subsequent reports and *www.mpikg.mpg.de/th/*

Reinhard Lipowsky
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The Power of Polypeptides from a Molecular Perspective

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Thesis: Computer based renormalization group study of the two-dimensional XY model
1997: Software trainee (TECMATH GmbH, Kaiserslautern)
1998-1999: Software engineer (LMS Durability Technologies GmbH, Kaiserslautern)
2003: PhD, Physics (MPI of biophysical chemistry, Göttingen)
Thesis: Mechanical coupling via the membrane fusion SNARE protein syntaxin 1A: a molecular dynamics study
2003-2005: Postdoc (University of Groningen, the Netherlands)
2005-2006: Postdoc (MPI of Colloids and Interfaces, Potsdam)
Since 2006: Group Leader (MPI of Colloids and Interfaces, Potsdam)

Polypeptides (also called proteins) are linear biopolymers composed of amino acid residues that fold into well-defined structures depending on their amino acid sequence. Folding is essential for the function of a protein whereas misfolding can cause severe diseases. Our aim is to understand protein function and diseases on a molecular level. The information on the molecular dynamics of polypeptides accessible experimentally is very limited. Therefore we employ molecular dynamics (MD) simulation techniques to model the process by which polypeptides sample conformational space. Here, the polypeptide and its solvent environment are described in atomic or near-atomic detail. Currently we try to understand how polypeptides may drag cellular organelles along filaments, recognize and kill bacteria as part of the immune defense, or cause neurodegenerative diseases.

Amyloid Peptides – Origin of Neurodegenerative Diseases

Amyloid diseases including Alzheimer's or Creutzfeld-Jakob disease are associated with the conversion of a protein from a soluble (functional) form into higher order fibrillar aggregates rich in β-sheet structure. The toxic species, though, seemingly, are not the mature fibrils but early oligomers. To understand the origin of their toxicity and to develop drugs against amyloid diseases requires to comprehend the structure of these species. We study the folding and aggregation of small amyloid peptides in solution. The systems investigated include the model amyloid peptide B18 as in **Fig. 1**(a,b) **[1]**, as well as the 25-35 **[2]** and the 10-35 fragment of the Amyloid β (Aβ) peptide associated with Alzheimer's disease **[3]**, as in **Fig. 1**(c-e) and (f-k), respectively.

The amyloid peptides form various β-sheets consisting of different sets of residues with comparable statistical weight. Aggregation is largely driven by the hydrophobic effect. Disordered conformations are stabilized entropically whereas fibril-like, β-sheet rich structures exhibit a lower energy. The Aβ (10-35) dimers show a larger conformational diversity than observed in previous simulations using a (less accurate) implicit solvent model, highlighting the need of the (more accurate but also computationally more expensive) explicit solvent model. In a running project, we also study the full length Aβ (1-40) peptide in terms of the effect of an interface on the peptide's conformation and the peptide's ability to induce membrane pores, as a possible origin of its toxicity. In collaboration with Gerald Brezesinski, the structure of larger aggregates, peptide monolayers with β-sheet structure at a water/air interface, has been studied **[4]**.

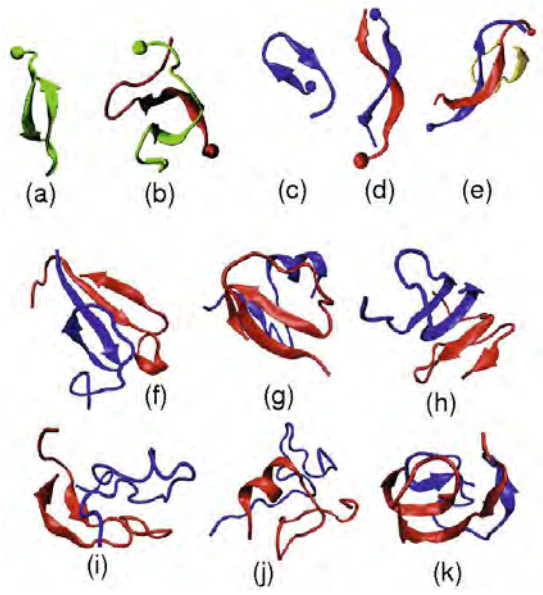

Fig. 1: β-hairpin folding and aggregation of fibrillogenic peptides in explicit water in molecular dynamics simulations. The model peptide B18 (a,b), as well as the Aβ (25-35) and Aβ (10-35) peptides associated with Alzheimer's disease, are depicted. In detail, (a) a B18 monomer **[1]** *and (b) dimer* **[1]**, *(c) an Aβ (25-35) monomer, (d) dimer* **[2]**, *and (e) trimer, as well as (f-k) Aβ (10-35) dimers* **[3]**, *are shown in ribbon representation.*

Antimicrobial Peptides – Smart Weapons of Immune Defense

Antimicrobial peptides (AMPs) are an evolutionary conserved component of the innate immune system found among all classes of life; their main function is the recognition and inactivation of invading pathogens like bacteria, viruses, or fungi. The mode of action of most AMPs is the permeabilization of the cell membrane via the formation of pores. AMPs are toxic against bacteria without affecting cells produced naturally in multicellular organisms, likely due to specific binding to lipids contained in the extracellular leaflet of prokaryotic but not eukaryotic cell membranes. In vitro experiments of the antimicrobial peptide NK-2 indicate that the discrimination between zwitterionic lipids with phosphatidylethanolamine (PE) head groups exposed by prokaryotes and phosphatidylcholine (PC) head groups exposed by eukaryotes plays an important role. We have conducted molecular dynamics simulations in conjunction with a coarse grained model confirming that NK-2 binds more strongly to PE than to PC and revealing the underlying mechanism **[5]**. As indicated in **Fig. 2**, we find that the transfer of NK-2 from POPE to POPC is favored because of a better shielding of nonpolar groups from the water and increased electrostatic interactions

between the cationic and anionic portions of the lipid headgroups. We also find that the adsorption of a cationic peptide to an anionic lipid is governed by a complex interplay of competing interactions. In a related project we reveal the driving forces of molecular recognition of pathogens in the form of proteins or lipids by antibodies **[6]**.

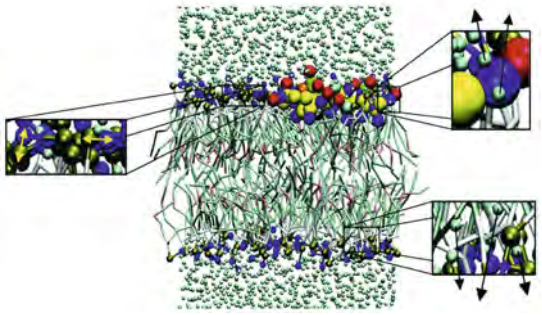

Fig. 2: Configuration of antimicrobial peptide NK-2 (large spheres) at a POPE bilayer from an MD simulation using a coarse grained model **[5]**. *The main contributions to the favorable transfer of NK-2 from POPE to POPC are highlighted; these are a removal of water particles from the hydrophobic core and the nonpolar side chains and an increase in the number of interlipid salt bridges.*

Molecular Motors – Force Generators of the Cell

Kinesin motors use the chemical energy supplied by ATP hydrolysis to transport cargo along microtubules (MTs). Because of the ATP hydrolysis, the motor assumes different nucleotide states during its processive motion. These three states differ in their affinities to the microtuble; strong binding of the motor domain to tubulin is observed when the nucleotide-binding pocket is empty or contains ATP whereas weak binding, leading to detachment, occurs when ADP is bound. The catalytic cycle of the motor domains is out-of-phase which facilitates kinesin's walk along the MT. Phosphate release is believed to trigger conformational changes in the motor head leading to detachment of the head from the MT and the undocking of the neck linker from the motor domain. The neck linker is a 10 amino acid residue peptide at the carboxy terminal of the motor domain and, because of its nucleotide dependent flexibility, is proposed to generate a force that brings the trailing motor head to the leading position.

Our simulations of a kinesin head attached to tubulin provide strong evidence for a specific allosteric coupling mechanism that consists of several subsequent molecular transitions which finally lead to the detachment of the neck linker from the motor domain **[7]**. The initial steps in this cascade of conformational changes induced by phosphate release are indicated in **Fig. 3**. Interestingly, our simulations reveal conformational changes of the proteins that are quite different from rigid-body transformations as previously assumed when high-resolution X-ray structures were fitted into low-resolution cryo electron microscopy images. In running projects we study the free energy differences between the different nucleotide states assuming a local equilibrium for pairs of states. As the motor energetics depend on the equilibrium constant for the hydrolysis reaction which we would like to understand from ab initio calculations, we are currently testing quantum mechanical methods, starting with the calculation of free energies of formation for gas phase reactions of small molecules. Finally, we investigate the mechanical step itself in full atomic detail with explicit solvent.

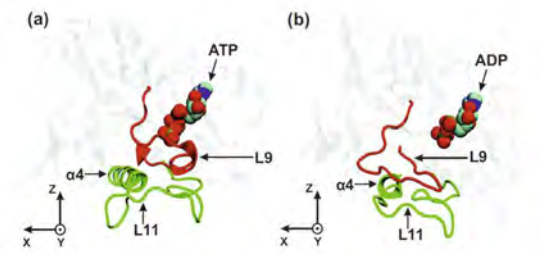

Fig. 3: Dominant conformations of the loops L9 (red) and L11 (green) for kinesin KIF1A attached to tubulin with (a) ATP and (b) ADP in the binding pocket, as obtained from MD simulations **[7]**.

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References:

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[2] Madeleine Kittner, Volker Knecht: Disordered versus fibril-like amyloid β (25–35) dimers in water: structure and thermodynamics. J. Phys. Chem. B, 2010, **114**, 15288.

[3] Madeleine Kittner, Alan Mark, Volker Knecht: Structure of Amyloid β (10-35) dimers in water. In preparation.

[4] Volker Knecht, Annabel Muenter-Edwards, Hans Börner, Gerald Brezesinski: Peptide monolayer with β-sheet structure at water-air interface probed by experiment and simulation. In preparation.

[5] Carola von Deuster, Reinhard Lipowsky, Volker Knecht: Specificity in binding of antimicrobial peptide to bacterial-like membrane based on hydrophobic effect and intramembrane electrostatics. Submitted.

[6] Parimal Kar, Reinhard Lipowsky, Volker Knecht: Importance of polar solvation for cross-reactivity of antibody and its variants with steroids. Submitted.

[7] Aliaksei Krukau, Volker Knecht, Reinhard Lipowsky: Conformational changes of ATP hydrolyzing enzymes from atomistic simulations: Kinesin's motor domain as a case study. Submitted.

Discrete Energy Landscapes of Proteins

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1996: Diploma, Physics
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Thesis: Interactions of rigid membrane inclusions
1999: PhD, Physics
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Thesis: Adhesion of multicomponent membranes
2000-2002: Postdoc
(University of California, San Francisco)
Since 2002: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)
2008: Habilitation, Physics
(University Potsdam)
Thesis: Transition states and loop-closure principles in protein folding

Continuous Versus Discrete Energy Landscape

A central goal in protein science is to characterize the free-energy landscapes of folding and binding. Such landscapes result from assigning free energies to all relevant conformations of a protein in a folding or binding process. If the conformations of a protein are described by the Cartesian coordinates of all its atoms, or by internal rotational degrees of freedom, the resulting free-energy landscapes are continuous and high-dimensional. These high-dimensional continuous landscapes have helped to understand general aspects of protein folding and binding (see **Fig. 1**). However, because of their complexity, they are difficult to apply in practice, i.e. to particular proteins or processes. Practical applications of continuous landscapes usually require projections on one or two 'reaction coordinates'. But the choice of such reaction coordinates is often arbitrary, and the projections may hide important aspects of the folding or binding dynamics.

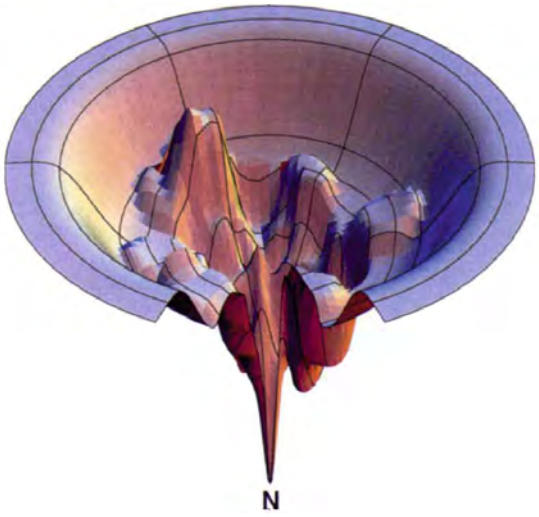

Fig. 1: Three-dimensional cartoon of a high-dimensional, continuous free-energy landscape of protein folding. The folded, 'native' state N of the protein corresponds to the global minimum on this landscape (from Dill, K. A. and Chan, H. S., Nat. Struct. Biol. 4, 10 (1997)).

To overcome these inherent problems of continuous free-energy landscapes, we have explored discrete landscapes of protein folding and binding in the past years **[1,2,3,4]**. A particularly promising approach is to construct detailed, discrete free-energy landscapes from simulation trajectories **[1]**. The discrete landscapes assign free energies and transition probabilities to a large but finite number of conformational states. These landscapes constitute detailed Markov models of folding or binding.

Discrete Landscapes from Molecular Simulations

Characterizing the equilibrium ensemble of folding pathways is one of the main challenges in protein folding. In principle, this ensemble of pathways is accessible via all-atom molecular dynamics simulations. But in practice, the ensemble is difficult to compute since the affordable simulation times are typically not sufficient to observe a significant number of folding events, unless largely simplified protein models are used. We have suggested a novel approach that allows to reconstruct the ensemble of folding pathways from simulations that are much shorter than the folding time **[1]**. This approach is based on (1) partitioning the state space into small conformational states, (2) constructing a discrete energy landscape, or Markov model, and (3) identifying transition pathways from the unfolded to the folded conformational states.

The first step in this approach involves a clustering of all conformations along the simulation trajectories into typically thousands of conformational states. In the second step, the transition probabilities between these conformational states are estimated from the numbers of transitions observed on the trajectories within a reasonably chosen 'lag time' Δt. The conformational states and transition probabilities represent a discrete landscape, or Markov model, of the folding process.

We have applied this approach to a set of 180 atomistic molecular dynamics trajectories of the Pin WW domain in explicit solvent **[1]**. The length of each of these trajectories is about two orders of magnitude shorter than the folding time of this protein. However, by jointly analysing these 180 trajectories, which 'explore' different regions of the energy landscapes, the folding pathways can be reconstructed, despite the fact that no contiguous pathway from the unfolded to the folded state is observed in a single simulation.

Folding Pathways and Folding Flux

To characterize the folding pathways in the third step of our approach, we have to identify conformational states on the energy landscape that correspond to the folded and the unfolded state of the protein. All remaining conformational states on the landscape are partially folded, intermediate states. The central quantity to characterize the folding pathways is the folding probability of these intermediate states. The folding probability of an intermediate state is the probability for reaching the folding state prior to the unfolded state. This folding probability, or 'committor', defines a direction on the energy landscape along which the folding flux between pairs of states can be computed. In a coarse-grained representation, the resulting folding flux for the PIN WW domain is depicted in **Fig. 2**. An interesting aspect of the PIN WW folding dynamics are metastable 'traps' in which the two β-hairpins of this protein are incorrectly folded.

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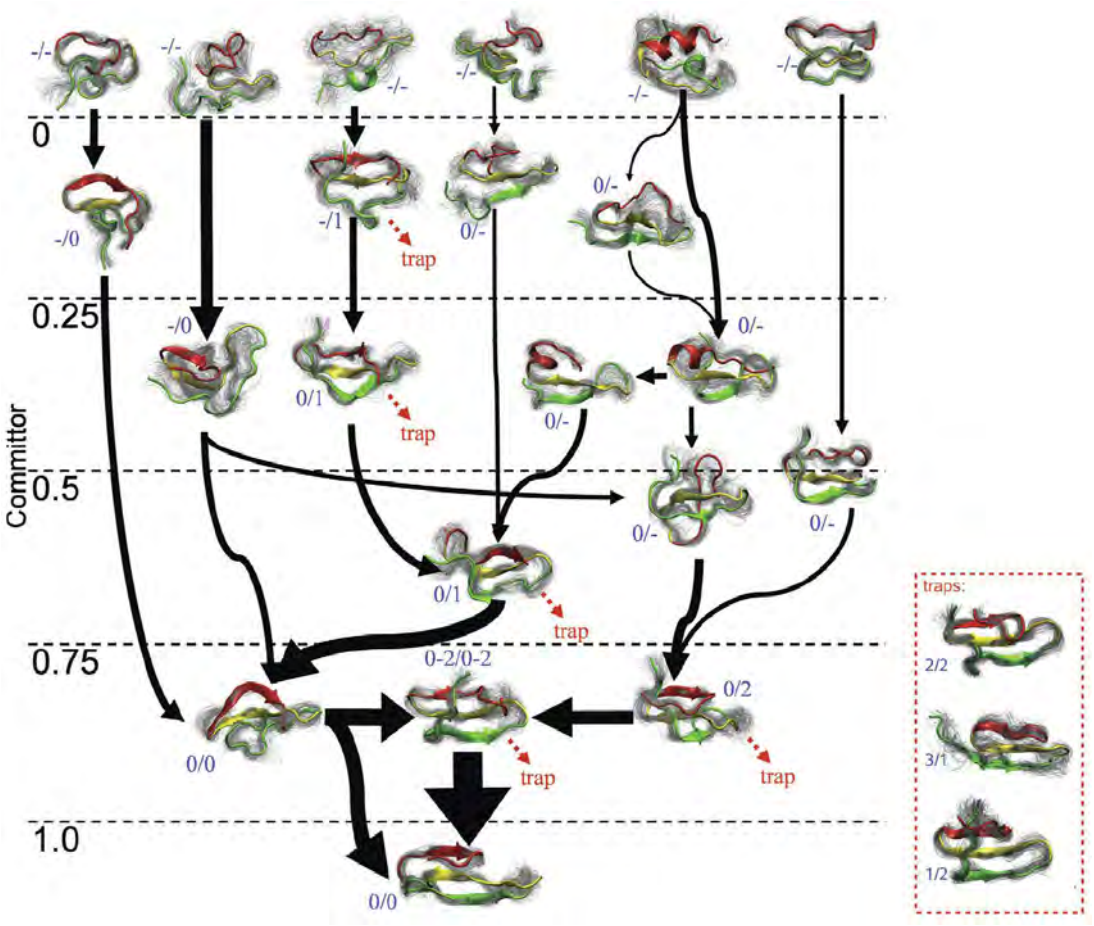

Fig. 2: Discrete landscape for the folding of the PIN WW domain. The folded structure (bottom) of this protein consists of two β-hairpins that form a three-stranded β-sheet. In this diagram, the unfolded state of the protein is represented by six conformational states (top). The numbers on the left indicate the committor probability, or folding probability, of each state. For each conformational state, a representative mean structure is shown in color, along with an overlay of equilibrium-distributed structures in this state to indicate the structural flexibility (gray cloud). The black arrows represent the probability flux between the states in folding direction. Besides 'correct' hydrogen bond alignments, or 'registers', in the two hairpins, we observe also conformational states in which these hydrogen bond registers are shifted by one or two residues compared to the folded state. The blue numbers next to the structures indicate whether the first/second hairpin has the native register (0), is register-shifted by one or two residues (1,2) or is not formed at all (-). Some of these register-shifted states are 'traps' without significant folding flux (lower right).

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Nanoparticles and Polymer Brushes

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Polymer brushes, i.e. polymers densely anchored to an interface have received much interest because of their scientific and technological importance. In good solvents the polymers are stretched away from the grafting plane causing a steep density gradient at the rim of the brush. Brushes consisting of two or more incompatible components are of special interest because they exhibit phase separation on nanometer scales. Morphological transitions and microphase separation are driven by immiscibility and/or contrast in solvent affinity. Lateral segregation can lead to stable surface nanopatterns and enables surface tuning as well as "smart" surfaces that respond to some extent to external stimuli. One of the less understood and still challenging problems in polymer science is the behavior of hybrid systems composed of polymer brushes and nanoparticles. On the one hand, even a small amount of such additives may have strong effects on the brush layer. On the other hand polymer brushes can be used to control the organization of nanoparticles into larger aggregates. We use dissipative particle dynamics (DPD) simulations that models molecules in solution on a coarse-grained level **[1]** to study both the morphology of heteropolymer brushes and the organization of nanoparticles guided by polymer brushes. In our model, there are five different types of DPD beads: polymer A and B blocks (A, B), solvent (S), nanoparticles (P), and wall (W).

Nanoparticles at Homopolymer Brushes

In this situation, the polymer brush consists of solvophilic A blocks only. Polymer-insoluble nanoparticles immersed into the brush are treated as rather rigid aggregates composed of 9 DPD beads, which are interconnected by harmonic springs. They exhibit an almost spherical form. To minimize the penalty in surface energy they tend to aggregate. Exceeding a certain size these aggregates are expelled towards the brush-solvent interface. The equilibrium state depends on the polymer-nanoparticle-solvent interfacial tensions γ_{AS}, γ_{AP}, γ_{PS}. The DPD interaction parameters can be chosen such that the spreading coefficient $S = \gamma_{AS}-\gamma_{AP}-\gamma_{PS}$ is negative, i.e., nanoparticles do not wet the brush surface, while the entry coefficient $E = \gamma_{AS}+\gamma_{AP}-\gamma_{PS}$ is positive, i.e. nanoparticles are drawn into the polymer film. Under such conditions, theory predicts nanoaggregates that grow freely in one lateral direction only. In the second direction, the supporting brush restricts growth. Varying nanoparticle concentration ϕ, in nice agreement with the prediction, we find a crossover from a vertical cylinder shape at small ϕ over a horizontally oriented flattened sphere to a highly anisotropic baguette-like shape at large ϕ (see **Fig. 1**) **[2]**.

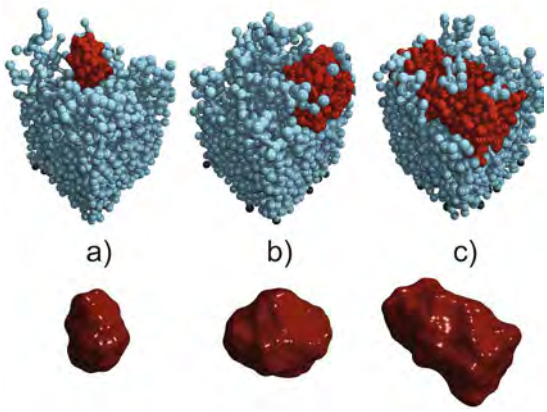

Fig. 1: Nanodroplets in the distal brush region at growing nanoparticle concentration ϕ (from left to right). Polymer beads are colored blue and nanoparticle ones red. Solvent beads are hidden. Bottom part: Connolly surfaces of the nanodroplets.

Surface Pattern of Diblock Copolymer Brushes

While macroscopic surface properties such as wettability and adhesion only depend on the average composition of the top layer on large length scales, the interaction of brushes on nanoscales is governed by the details of its morphology. To make substantial progress with applications based on polymer pattern on nanoscales, a detailed understanding of the microphase separation in multiblock brushes is of fundamental importance. We study tethered diblock copolymers in selective solvents where the chains are anchored via the ends of soluble A blocks while the solvent is poor for B blocks. Under such conditions, A blocks form stretched brushes whereas insoluble B blocks exhibit different morphologies, which depend both on solvent quality $\tau_B = a_{BS}/a_{BS}^{(0)} - 1$, where a_{BS} is the DPD parameter setting the repulsion between B blocks and solvent, and on chain composition $f_B = N_B / (N_A + N_B)$, where $N_{A,B}$ are the lengths of A and B blocks, respectively. **Fig. 2** gives the morphology diagram in the $f_B - a_{BS}$ parameter space studied by simulations and **Fig. 3** shows typical simulation snapshots **[3]**. With increasing length of B blocks, in the top brush layer we obtain transitions from spherical B micelles (hexagonal phase) via cylindrical micelles (stripes) and spherical A micelles (inverted hexagonal) to a uniform lamella. This observation is in agreement with experimental findings. Note that we treat A-B incompatibility and solvent selectivity separately by two independent parameters a_{AB} and a_{BS}. Analyzing the micellar aggregates we found an unusual feature not obtained in previous one-parameter models. In **Fig. 4**, the average number of chains per spherical micelle is plotted as a function of solvent quality. Obviously it saturates at large τ_B or $a_{BS} > a_{AB}$. Supported by simulation snapshots this behavior indicates that the solvophobic B domains are covered by soluble A blocks to reduce unfavorable interactions with solvent.

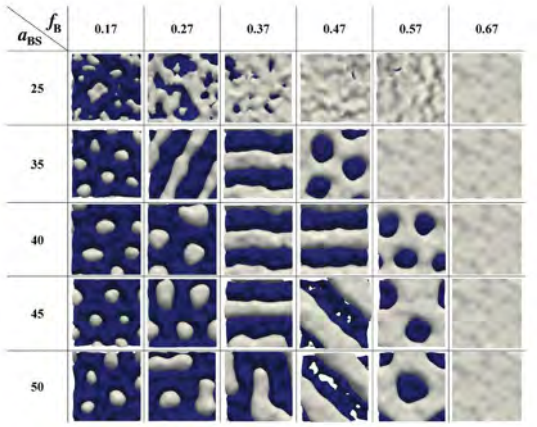

Fig. 2: Morphology diagram of diblock copolymer brushes in selective solvents in terms of polymer composition ϕ_B and solvent quality (interaction parameter a_{BS}). Shown is the top view of equidensity plots where A and B regions are colored dark and light grey, respectively.

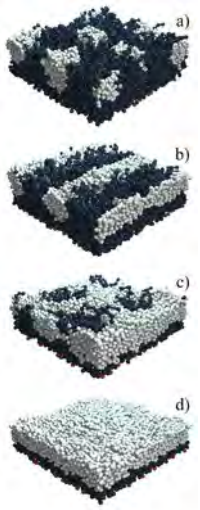

Fig. 3: Typical morphologies obtained at a_{BS}= 40 and varying polymer composition: a) f_B =0.17, b) 0.37, c) 0.57, and d) 0.67. Coloring similar to Fig. 2.

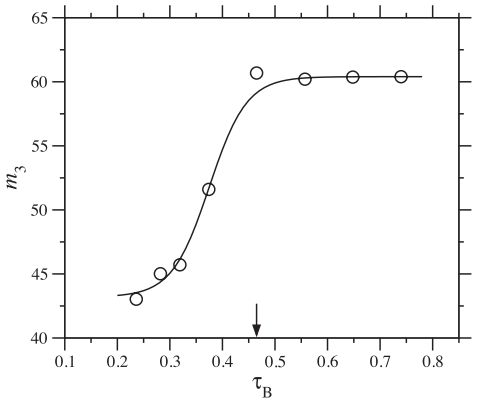

Fig. 4: Average number of chains per micelle versus solvent quality. The arrow indicates τ_B where a_{BS} equals a_{AB}. At $a_{BS} > a_{AB}$ the behavior becomes independent of solvent quality (see text).

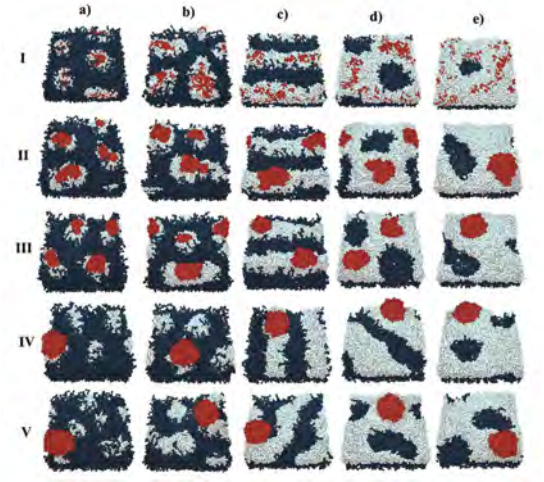

Fig. 5: Nanocomposite systems of diblock copolymer brushes and nanoparticles at different polymer composition with ϕ_B growing from left to right and variable interaction strength between nanoparticles and B blocks with a_{BP} growing from top to down.

Diblock Copolymers as Template for Nanoparticles

Beside the uninteresting laterally homogeneous lamella phase the morphology diagram shown in **Fig. 2** exhibits two major pattern types that can be used to establish templates for the organization of nanoparticles: (i) hexagonally packed dots and (ii) periodic line pattern. **Fig. 5** shows a typical brush-nanoparticle pattern diagram in the $\phi_B - a_{BP}$ space **[4]**. The constant parameters are $a_{AB}=a_{BS}=a_{PS}=a_{AP}=40$, $a_{AS}=25$, $\phi=0.112$. For $a_{BP}=25$ (row I), nanoparticles are soluble in B domains and aggregate inside those domains following their shape. In this case nanoparticles increase the effective B block fraction, which causes a corresponding shift in the morphology diagram of the underlying brush. For moderate a_{BP} (rows II, III), we obtain finite spreading of nanoparticle droplets along B regions. In the situation shown in **Fig. 5**, spreading is restricted because of the large surface tension due to $a_{PS}=40$. For large $a_{BP}>40$ (rows IV, V), nanoparticles form a single droplet on the top of a B domain. **Fig. 5** illustrates the complex challenge to use diblock copolymer brushes as soft templates for nanoparticle organization. However, numerical simulations offer a powerful tool to detect and to analyze the most interesting regions of the huge parameter space.

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Conformational Dynamics of Complex Oligosaccharides

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The operation and stability of many types of biomolecules in the extracellular matrix are influenced by the presence of attached carbohydrate residues. The specific function of these sugar components and thus their potential, e.g., for developing novel vaccines, are to a large extent unknown.

Systematic exploration of *glycans* is difficult in general. Experimental access is mostly limited to solution NMR, and on the numerical side, the abundance of different types of glycosidic linkages inhibits the development of generalizable force fields suited for molecular dynamics (MD) simulations.

In this situation, *invariant* carboydrate components may serve as a starting point for a more concise investigation. The backbone of the so-called Glycosylphosphatidylinositol (GPI) anchor that covalently binds many types of proteins to cell membranes, is an example of such a recurrent core structure.

Atomistic Modelling of the GPI backbone

The whole molecule linking a protein to the cell membrane consists of several parts, see **Fig. 1**. An ethanolamine residue links the protein to a backbone carboydrate sequence which connects via an inositol ring and a phosphate group to a fatty acid immersed in a cell membrane **[1]**. The whole GPI anchor is expressed in a large number of variations, phosphate groups and/or further oligosaccharides being attached to the hydroxyl groups of the backbone. A prototypical question to ask here is: what kind of characteristic overall structure does the backbone maintain?

To model the backbone atomistically, we employ an all-atom bio-molecular force field particularly devoted to carbohydrates **[2]**. It is also sufficiently generalizable to adopt a strategy of independently considering various fragments of the backbone. This facilitates comparison with detailed NMR studies (2D-NOE spectra of di- and tri-saccharide fragments) and also allows us to run long simulation trajectories on a single fragment: conformational dynamics significantly slows down because of the surrounding aqueous solution which must be modeled explicitly, since many hydroxyl groups maintain a complicated network of hydrogen bonds with solvent water molecules.

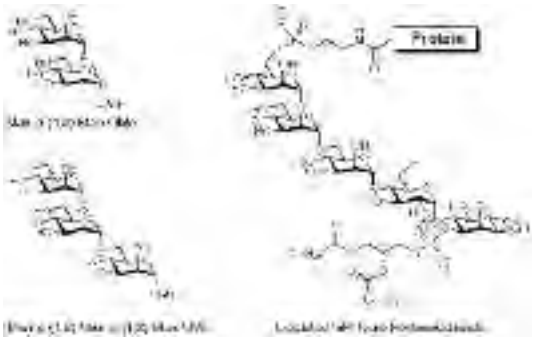

Fig. 1. GPI-core structure in its simplest configuration (right). The backbone consists of 4 sugars and one inositol ring. For detailed experimental (NMR) and theoretical (MD) analysis, the backbone can be decomposed into adequate subunits, two of which are to the left. The chemical structure formulas only indicate the molecule topology, not the actual geometric conformation.

Dynamics of Glycosidic Linkages

Because single sugar rings are relatively rigid, the conformational preferences of an oligosaccharide can be characterized in much the same way as torsion angles within a peptide backbone. In **Fig. 2**, the disaccharide 1-6-linkage, central to the backbone, is shown. The overall dihedral dynamics is revealed only with long (100ns-1µs) MD-simulations. The glycosidic angle trajectories reveal the different time scales involved. Whereas during periods up to several tenths of nanoseconds a conformation corresponding to one particular value of omega may appear very stable, on a time scale one order of magnitude larger the picture changes completely. On yet larger timescales, the molecule thus appears quite flexible. For the backbone, it might even turn out that it can rather be viewed as a flexible chord, particular conformational preferences loosing their significance **[3]**.

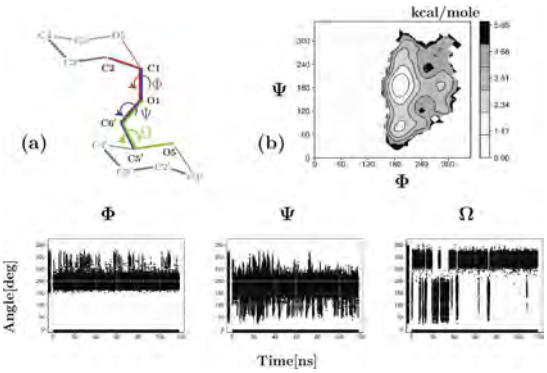

Fig. 2. (a) Definitions of dihedral angles for a 1-6 linkage between two mannoses (exocyclic groups omitted). Lower ring is the reducing end (primed). (b) Frequency distribution of Phi-Psi occurrences, converted to energy units (histogram assembled from 240.000 data points during a 120ns simulation). Lower panel: trajectories of the three glycosidic dihedral angles taken from the same simulation run.

Characterising Oligosaccharides on a Monomer Basis

Complementary to a "per linkage" point of view is to consider the oligosaccharide on a "per monomer" basis. One may ask which properties of a monosaccharide unit, apart from possible linkages to others, may favor its occurrence in a certain oligosaccharide. To tackle this question one may simply start with looking at differences across a stereo-chemical series. For a certain subset of aldohexoses the chemical formula is the same, yet they differ in orientation of their hydroxyl groups. In a preliminary studies we are considering mannose and glucose, deviating only in the orientation of their hydroxyl group at the C2 carbon atom. Within our atomistic model, we have used thermodynamic integration to grow glucose into mannose in solution as well as in vacuum, the differences of these values determining the variation in solvation free energy between the two molecules **[4]**. Especially in vacuum the analysis is complicated by the trapping of hydroxyl and hydroxy-methyl conformations, resulting in large and strongly varying error bars, see **Fig. 3**. No standard procedure is available to meet this situation. In our case one has to force the molecule to go along a smoother path between the initial and final state, a procedure that finally leads to a respectable difference of 1.8 kcal/mole between the two species.

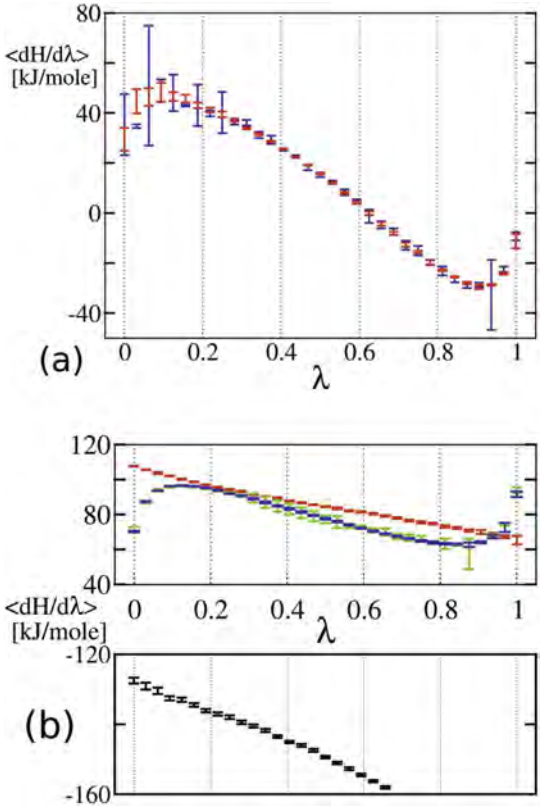

Fig. 3. Behavior of the derivative of the internal energy <H (λ)> with respect to the thermodynamic integration parameter λ, for two distinct paths leading from Glucose (λ=0) to Mannose (λ=1) in vacuum. (a) all parts of the molecular Hamiltonian vary simultaneously (blue: 1.6ns simulation time per data point, red: 16ns). (b) Before changing the molecular topology, charges on hydroxyl hydrogens are absorbed into their oxygen atoms (red). At least for the simulations with 16ns per data point (blue), we can achieve a smooth variation with relatively small error bars. The lower panel in (b) shows the contribution to the free energy change, when all remaining charges are restored (last part of the graph omitted for clarity).

The general type of difficulty met here is similar to the dynamical study of the backbone. Averages of any kind of observables are strongly influenced by a series of closely spaced conformers.

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Membranes, Ions, and Water at the Molecular Level

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The function of biomembranes is not restricted to surrounding a cell and its various compartments as inert 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 experimentally accessible information about the molecular architecture of membranes is very limited. Therefore, we use molecular dynamics simulation techniques to study the cooperative processes underlying the mesoscopic properties of membranes. As a first step, we model membranes as lipid bilayers.

Membranes and Ions

A biomembrane in vivo is surrounded by an aqueous solution containing ions. The most abundant atomic monovalent ions are potassium (K^+), sodium (Na^+), and chloride (Cl^-). Sodium and potassium can be specifically adsorbed at membranes as indicated from various experimental and simulation studies, the membrane affinity being somewhat higher for Na^+ than for K^+. In order to model interactions of ions with a membrane, a reliable force field is required but a force field for K^+ in conjunction with the widely used simple point charge (SPC) model for water has not been available.

We have derived a force field for K^+ matching activity coefficients of aqueous KCl solutions for a wide range of concentrations, as shown in **Fig. 1 [1]**. The figure also shows that the solution activities of other force fields significantly deviate from the experimental values. Our force field for KCl is shown to also reproduce the experimental binding constant for the adsorption of K^+ at a POPC bilayer as shown in **Fig. 2 [2, 3]**.

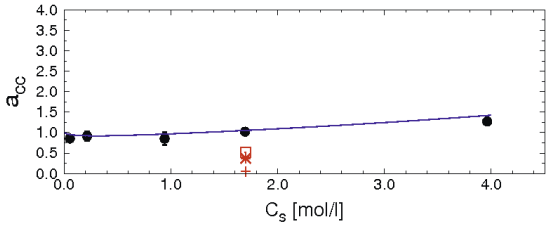

Fig. 1: Activity derivative of aqueous KCl solutions as a function of the molar KCl concentration **[1]**. *The line shows a fit to the experimental data, the black circles indicate the results for our KCl force field with simple point charge (SPC) water, and the red symbols show the results for force fields from the literature.*

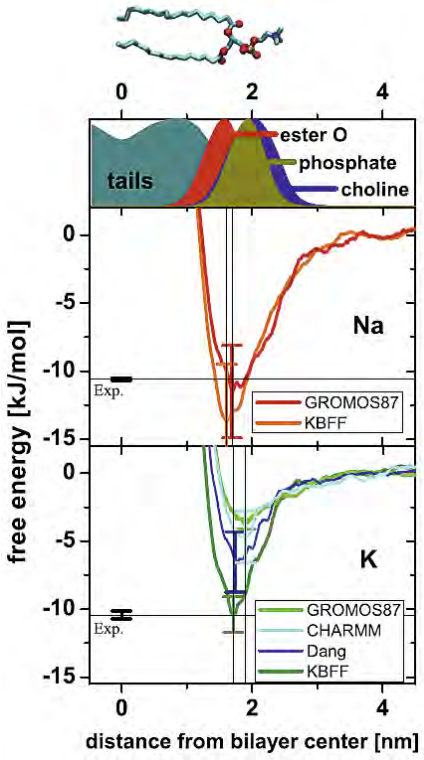

Fig. 2: Free energy as a function of the distance of sodium or potassium from the center of a POPC bilayer for different ion force fields **[2]**. *The horizontal lines show the experimental adsorption free energies (Exp.)* **[3]** *for the respective cation chloride. The distribution of various atomic groups normal to the bilayer and a representative lipid configuration are shown as a reference.*

In contrast, models used in previous simulation studies are found to underestimate the membrane affinity of K^+, thus exaggerating the difference between Na^+ and K^+. Our simulations support the view that ion adsorption at PC membranes is driven by an entropy gain due to the release of hydration water from the ions and the lipids.

The interaction of ions with membranes also affects the tendency of membranes to fuse with one another, a key step in intracellular traffic, viral infection, and liposome-mediated drug delivery. The latter is achieved by pH-responsive liposomes. One important component of such systems is cholesteryl hemisuccinate (CHEMS) being negatively charged and forming stable liposomes above pH 6 and being neutral below pH 5 where it becomes fusogenic. Our MD simulations explain this behavior showing strong binding of counterions to anionic CHEMS and counterion release for neutral CHEMS

as shown in **Fig. 3**. Counter ion release is found to correlate with a decrease in the effective headgroup size known to promote fusion **[4]**.

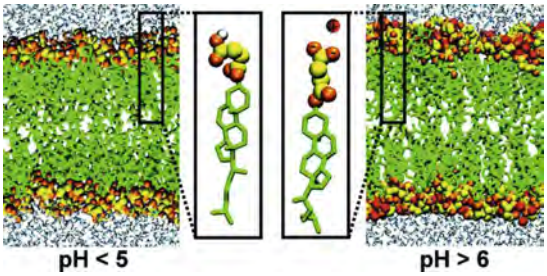

Fig. 3: Cutout cross sections of hydrated CHEMS bilayers in (left) protonated state and (right) deprotonated state with sodium, the insets showing individual CHEMS molecules **[4]**.

Membrane Fusion

The fusion of two membranes requires the approach of the membranes, the latter being hindered by strong repulsive hydration forces. We have computed the hydration forces between two POPC bilayers using a coarse grained model and get good agreement with experimental values. Our results suggest that, unlike suggested previously, the directionality of hydrogen bonds between the lipids and water, not described in our model, is not essential for the occurrence of hydration forces **[5]**.

Once two membranes are close to each other, the hydration forces can be circumvented by the formation of small defects which can lead to the formation of so-called "stalks" between the two bilayers formed by multiple lipids. Our simulations show that such defects are related to the exposure of hydrophobic lipid tails to the water, as shown in **Fig. 4 [6]**. Peptides derived from the fusion hemagglutinin fusion protein of the influenza virus and denoted as fusion peptides, known to induce membrane fusion in vitro, do not accelerate stalk formation and even increase the hydration forces, thus not facilitating fusion kinetically. However, they can stabilize stalk-pore complexes thermodynamically as shown by self-assembly, leading to a new, so-called simple cubic phase, induced by the peptides **[7]**. We do find that fusion peptides strongly stabilize membrane nanopores, in good correlation with experiments. Even in the absence, though, membrane nanopores are kinetically stabilized by a small energy barrier, as we have revealed from atomistic simulations **[8]**.

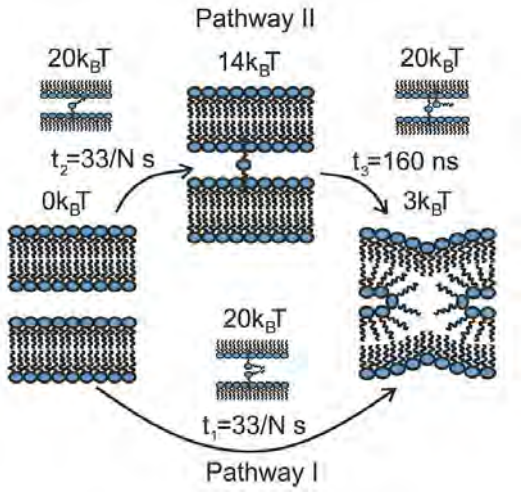

Fig. 4: Early membrane fusion energetics and kinetics for two POPC bilayers separated by five waters per lipid **[6]**. *The symbol N denotes the number of lipids in the proximate leaflets.*

Electrokinetic Phenomena

Hydrophobic surfaces in water are widely believed to adsorb hydroxide (OH^-) ions. This is suggested by the fact that oil droplets in water exposed to an electric field move as if they were negatively charged (i.e., they exhibit negative electrophoretic mobilities). However, we have performed MD simulations using an all-atom polarizable potential reproducing the sign and the size of the electrophoretic mobilities of oil in water although ions were absent, as indicated in **Fig. 5 [9]**. The underlying mechanism is related to the polarization of the water and the oil at the interface. Our results may help to resolve a current controversy concerning the charge of hydrophobic surfaces in water. Interestingly, non-classical electrokinetic phenomena - in the form of charge inversion - also occur in biology, playing a role in the function of kidney and related diseases **[10]**.

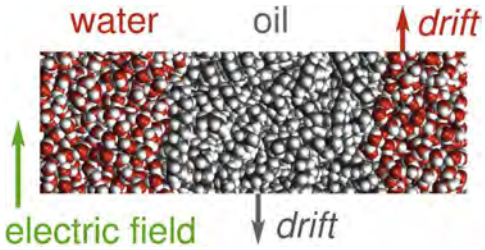

Fig. 5: An electric field applied parallel to a water/oil interface induces a tangential movement between the phases **[9]**. *The effect requires a sufficiently detailed model describing not only the water but also the oil in full atomic detail and using a polarizable interaction potential.*

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Binding Cooperativity of Membrane Adhesion Receptors

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Cell adhesion processes are essential for the distinction of self and foreign in immune responses, the formation of tissues, or the signal transduction across the synaptic cleft of neurons. The adhesion processes are mediated by the specific binding of receptor and ligand proteins anchored in the cell membranes. Because of the importance of these processes, the binding of cells to other cells or to surface-supported lipid membranes with anchored ligand molecules (see **Fig. 1**) has been studied intensively.

Binding Affinity of Receptors and Ligands

A central question is how to characterize and measure the binding affinity of the membrane-anchored receptor and ligand molecules that are involved in cell adhesion. For *soluble* receptor and ligand molecules, the binding affinity can be characterized by the binding equilibrium constant K_{3D}, defined by

$$[RL]_{3D} = K_{3D}[R]_{3D}[L]_{3D} \quad (1)$$

where $[RL]_{3D}$ is the volume concentration of bound receptor-ligand complexes, and $[R]_{3D}$ and $[L]_{3D}$ are the volume concentrations of unbound receptors and unbound ligands in the solution. The equilibrium constant K_{3D} is determined by the binding free energy of the complex and can be measured with standard experimental methods.

An often considered two-dimensional analogue for *membrane-anchored* receptors and ligands is the quantity

$$K_{2D} = \frac{[RL]}{[R][L]} \quad (2)$$

where [RL], [R], and [L] are the *area* concentrations of bound receptor-ligand complexes, unbound receptors, and unbound ligands. However, different experimental methods to measure K_{2D} lead to values that differ by several orders of magnitude, which indicates that K_{2D} is not a proper constant **[1]**.

Membrane Fraction within Receptor Binding Range

Quantifying the affinity of membrane-anchored receptor and ligand molecules is complicated by the fact that the binding process depends on the local separation and, thus, the conformations of the two apposing membranes. A receptor molecule can only bind an apposing ligand if the local membrane separation is comparable to the length of the receptor-ligand complex. A central quantity therefore is the fraction P_b of the apposing membranes with a separation within the binding range of the receptor-ligand interaction. The concentration of bound receptor-ligand complexes

$$[RL] = P_b K_b [R][L] \quad (3)$$

is proportional to P_b as well as to the concentrations [R] and [L] of unbound receptors and ligands **[1,2,4]**. Here, K_b is the well-defined two-dimensional equilibrium constant for membrane segments within the binding range of the receptors and ligands.

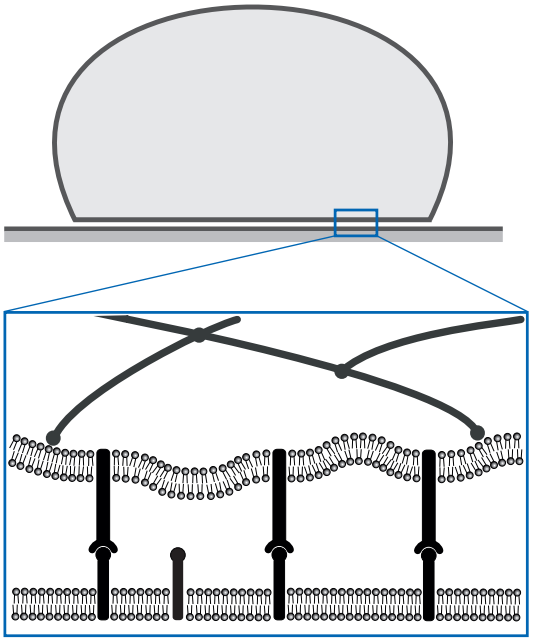

Fig. 1: A cell adhering to a supported membrane with anchored ligands that bind to receptors in the cell membrane. The binding of receptors and ligands in the cell adhesion zone is affected by membrane shape deformations and fluctuations on nanometer scales, which are dominated by the bending rigidity of the cell membrane. The adhesion receptors of immune cells are typically mobile along the membrane only weakly, coupled to the cytoskeleton, if at all.

Thermal shape fluctuations of the membranes on nanometer scales lead in general to values of P_b smaller than 1. For cell membranes, these nanometer scale fluctuations are not, or only weakly, suppressed by the cell cytoskeleton, in contrast to large-scale shape fluctuations.

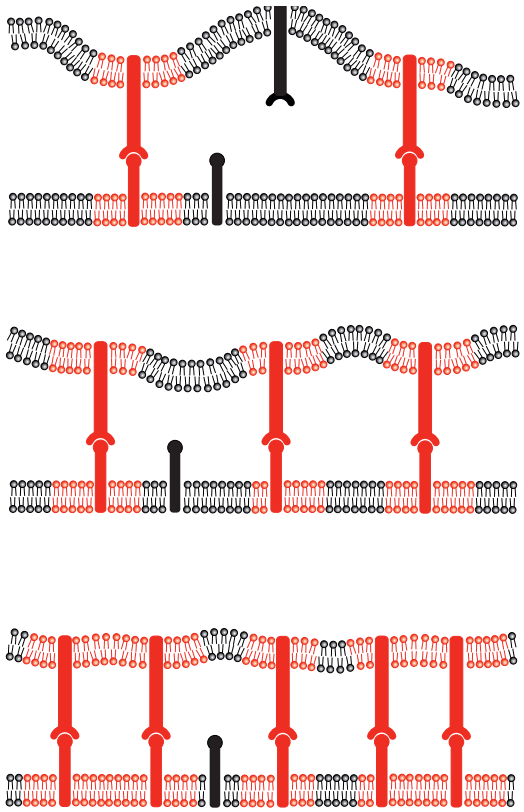

Fig. 2.: An important quantity is the area fraction P_b of the membranes within binding separation of the receptors and ligands. The area fraction P_b (shown in red) increases with the concentrations of receptors and ligands, since the formation of receptor-ligand bonds 'smoothens out' thermal membrane shape fluctuations. The 'smoothening' facilitates the formation of additional receptor-ligand bonds and, thus, leads to a binding cooperativity **[1,2,4]**.

We have developed a statistical-mechanical model of membrane adhesion in which the membranes are described as discretized elastic surfaces and the adhesion receptors and ligands as individual molecules diffusing on these surfaces **[2]**. In our model, the fraction P_b of the membranes within binding range of the receptors and ligands turns out to be much smaller than 1 for typical lengths and concentrations of receptors and ligands in cell adhesion zones. Scaling analysis and Monte Carlo simulations lead to the relation

$$P_b \approx c(\kappa/k_BT)l_{we}^2 K_b[R][L] \qquad (4)$$

which indicates that the membrane fraction P_b within the binding range of the receptors and ligands is proportional to $[R]$ and $[L]$. Here, $c \approx 13$ is a dimensionless prefactor, $\kappa = \kappa_1\kappa_2/(\kappa_1 + \kappa_2)$ is the effective bending rigidity of the two apposing membranes with rigidities κ_1 and κ_2, k_BT is Boltzmann's constant times temperature, and l_{we} is the interaction range of the receptor-ligand bonds.

Cooperative Binding of Membrane Receptors

A direct consequence of the equations (3) and (4) is the quadratic dependence

$$[RL] \approx c(\kappa/k_BT)l_{we}^2 K_b^2 [R]^2[L]^2 \qquad (5)$$

of the bond concentration $[RL]$ on the area concentrations $[R]$ and $[L]$ of free receptors and ligands. This quadratic dependence indicates cooperative binding. The binding cooperativity results from a 'smoothening' of the thermally rough membranes and, thus, an increase of P_b with increasing concentrations $[R]$ and $[L]$ of receptors and ligands, which facilitates the formation of additional receptor-ligand complexes (see **Fig. 2**).

A consequence of eq. (5) is that the quantity K_{2D} defined in eq. (2) is not constant, but depends on the concentrations of the receptors and ligands. Eq. (5) thus helps to understand why different experimental methods to measure K_{2D} can lead to significantly different results **[1]**.

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Aqueous Phase Separation in Vesicles: Wetting Phenomena and Nanotube Formation

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Aqueous solutions containing two species of water-soluble polymers such as dextran and polyethylen glycol (PEG) undergo phase separation as soon as the polymer concentrations exceed a few weight percent, see **Fig. 1**. Membranes and vesicles suspended in such a solution are then exposed to two different aqueous phases. Such lipid/polymer systems undergo complete-to-partial wetting transitions **[1]**, exhibit effective and intrinsic contact angles **[2]**, and lead to the formation of membrane nanotubes **[3]**.

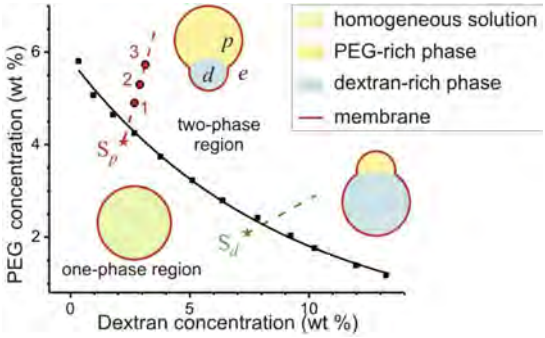

Figure 1: Phase diagram of aqueous solution of PEG and dextran. The solution undergoes phase separation into a PEG-rich phase p *and a dextran-rich phase* d *as soon as the concentration of one of the polymers exceeds a few percent. The black line represents the binodal, i.e. the boundary between the one-phase and the two- phase region. The red and the green lines indicate two different deflation trajectories starting from two initial states* S_p *and* S_d *in the one phase region.*

A convenient method to induce phase separation within the vesicles is by osmotic deflation. Osmotically active particles such as sugar molecules are added to the exterior solution, and the resulting osmotic unbalance leads to the permeation of water through the vesicle membranes and to a reduced volume of the vesicles. Since the dissolved polymers cannot permeate the membrane, the polymer concentration is increased, and the aqueous solution within the vesicle forms two separate phases, a PEG-rich and a dextran-rich phase, see **Figs. 2** and **3**.

In **Fig. 2**, the aqueous solution within the vesicle is initially homogeneous, see **Fig. 2(a)**, and then forms, during successive deflation steps, a dextran-rich droplet (light green) and a PEG-rich droplet (dark green), see **Fig. 2(b) - (f)**.

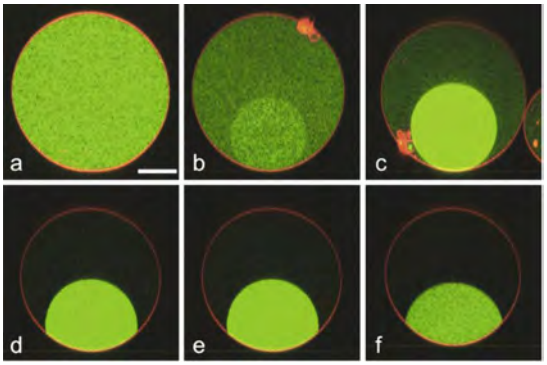

Figure 2: Confocal micrographs of a lipid vesicle (red line) which encloses a PEG- rich droplet (dark green) and a dextran-rich droplet (light green). As the vesicle is deflated from (c) to (d), the membrane undergoes a transition from complete to partial wetting by the PEG-rich phase. Further deflation from (d) to (f) leads to an increasing value of the contact angle between the membrane and the PEG-rich phase. Scale bar: 20 µm. ***[1]***

Inspection of **Fig. 2** shows that the contact angle between the PEG-rich droplet and the membrane is close to zero for small deflation as in **Fig. 2(b)** and **(c)** but starts to increase for larger deflation as in **Fig. 2(d) - (f)**. Therefore, the system undergoes a complete-to-partial wetting transition as the vesicle is deflated from **Fig. 2(c)** to **(d)**.

The vesicle shapes shown in **Fig. 2(d) - (f)** are somewhat special since they stay essentially spherical even though the membrane is partially wet by both phases. In general, partial wetting of the membrane leads to a kink along the contact line, at which the membrane is pulled by the interface between the PEG-rich and dextran- rich phase, see **Fig. 3(a)**. In all cases, this contact line divides the membrane into two distinct segments, separating the two aqueous phases, α and β, within the vesicle interior from the exterior solution, γ. In general, these two membrane segments experience two

distinct mechanical tensions, $\Sigma_{\alpha\gamma}$ and $\Sigma_{\beta\gamma}$. In mechanical equilibrium, these two tensions must be balanced, along the contact line, by the interfacial tension $\Sigma_{\alpha\beta}$ between the two liquid phases, see **Fig. 3(a)** and **(b)**.

The kink shown in **Fig. 3(a)** is observed by optical microscopy but cannot persist to small length scales, since such a kink would imply an infinite bending energy of the membrane. Therefore, when viewed with suboptical resolution, the membrane must be smoothly curved as in **Fig. 3(b)**, which implies the existence of an intrinsic contact angle Θ_{in}. In contrast to the three contact angles shown in **Fig. 3(a)**, the intrinsic contact angle represents a material parameter that is independent of the vesicle geometry. **[2]**

Another unexpected aspect of the aqueous phase separation within the vesicles is the formation of membrane nanotubes, see **Fig. 4**. The tubes have a diameter below optical resolution and become only visible when fluorescently labeled. The tubes form during the phase separation process and are stable after this process has been completed **[3]**. A theoretical analysis of the deflated vesicles reveals that these membrane tubes are stabilized by negative spontaneous curvature. Using the large separation of length scales between the tube diameter and the overall size of the vesicles, the spontaneous curvature can be calculated and is found to be about - 1/(240 nm) for a certain range of polymer concentrations. The nanotubes can also be retracted back into the mother vesicle by increasing the membrane tension via micropipette aspiration of the vesicle.

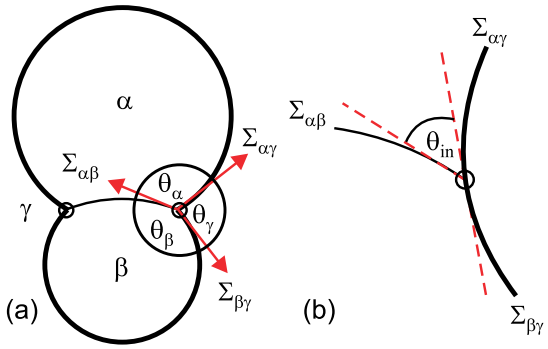

Figure 3: (a) Cross-section of a vesicle enclosing one α (top) and one β (bottom) droplet suspended in the exterior solution γ. When viewed with optical resolution, the vesicle shape exhibits a sharp kink along the contact line (⊙) and can be characterized by three effective contact angles Θ_α, Θ_β, and Θ_γ .These contact angles are related to the three tensions $\Sigma_{\alpha\beta}$, $\Sigma_{\alpha\gamma}$, and $\Sigma_{\beta\gamma}$ via the force balance along the contact line; and (b) Enlarged view close to the contact line: Intrinsic contact angle Θ_{in} between the two planes that are tangential to the α_β interface and to the smoothly curved vesicle membrane, respectively, at a certain point of the contact line. ***[2]***

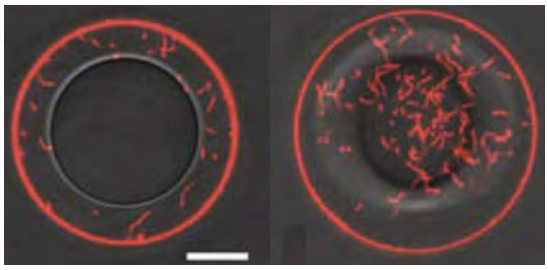

Figure 4: Membrane nanotubes (short red segments) extending from the vesicle membrane (red circle) into the vesicle interior. The nanotubes are below optical resolution and only visible when fluorescently labeled. These tubes are induced by the aqueous phase separation and stabilized by the spontaneous curvature of the membranes. The latter curvature is negative and about - 1/(240 nm). The tube may then have a cylindrical shape with radius 120 nm, a necklace-like morphology consisting of small spheres with a radius of 240 nm, or some intermediate morphology. ***[3]***

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Stochastic Processes in Complex and Biological Systems

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Molecular Motors as Semi-Markov Chains

Kinesin is a complex molecular machine whose properties have been studied in great detail both theoretically and experimentally in our department **[1, 2]**. When we experimentally observe a kinesin molecule walking along a filament, we see a series of forward and backward steps, whose relative frequency depends on the availability of ATP, the fuel of this motor. A more detailed analysis reveals, however, that the steps of the kinesin motor are more complex. In fact, both the probability of a motor to make a step forward or backward and the time that it takes to perform one of these steps depend on whether the motor had previously performed a forward or backward step. A detailed analysis of these different probabilities was done in **[3]**, where we showed that the motor's displacements should be described in terms of pairs of steps, such as bf which means a step backward followed by a step forward. It turns out, therefore, that there are four such states indicated as *{ff, fb, bf, bb}*. In this representation, the motor is described as a stochastic chain in continuous time over these four states with the property that the dwell times are not exponentially distributed. These chains are called semi-Markov chains. Since the dwell times on these four states are also experimentally accessible and this level of description may apply to a large class of motors, we want to develop a mathematical framework to analytically compute several properties that are also easily accessible experimentally. This project is performed in collaboration with Prof Sylvie Rœlly at the University of Potsdam.

A. Valleriani, P. Keller, R. Lipowsky

Models for Translational Control

Translation of the messenger RNA (mRNA) is a key process in cell biology. The process of translation is performed by ribosomes, which are molecular machines walking unidirectional on the mRNA while synthesizing the proteins. The amount of proteins produced by each mRNA depends therefore on the number of ribosomes on it, which depends on the initiation rate, on the speed by which the ribosomes move along the chain, and on the termination rate. Finally, the number of ribosomes depends also on the life time of the mRNAs. Our work is mainly concerned with the bacterium *E. coli*. Experimentally, in collaboration with Prof Zoya Ignatova at the University of Potsdam, we are determining the number of ribosomes on certain mRNAs and we are preparing the samples for a ribosomal footprinting over the whole set of mRNAs in this organism. From the theoretical side, we have found out that the kind of mRNA degradation pathways in *E. coli* cells has some effect both on the number of ribosomes and also on the rate of protein synthesis and that this effect is stronger for longer mRNAs **[4, 5, 6]**. In our theory, simple models of mRNA degradation have shown that some differences in the process of degradation can have dramatic effects on the translation rate (see **Fig. 1**). We are therefore developing more complex models based on the available knowledge about the degradation process in order to finally understand the role of degradation on the rate of protein synthesis **[7]**. On the other hand, under certain circumstances the tRNAs necessary to perform the translation can become particularly rare and thus slow down the ribosomes at certain positions along the mRNA **[8]**. We are thus developing a model to take properly into account the effective concentrations of all tRNAs and thus predict the local speed of the ribosomes and compare these results with the experimental footprinting.

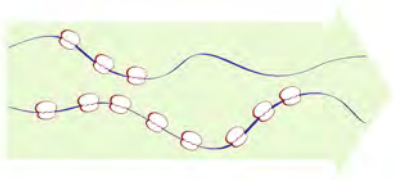

Fig. 1: Schematic diagram of mRNA translation at different times. The two chains have the same length but differ in the number of loaded ribosomes. The upper chain is young and has only few ribosomes that are close to the initiation region. The chain at the bottom is older and thus is loaded with more ribosomes. The arrow indicates the direction of motion of the ribosomes. If mRNA turn-over is very rapid, some mRNA may be degraded before producing any protein.

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Life Cycle of Chlamy Cells

Chlamydomonas reinhardtii (chlamy) is a unicellular photosynthetic alga that is studied within the ongoing systems biology project GoFORSYS, in collaboration with the University of Potsdam and the MPI of Plant Physiology (MPIMP). Chlamy cells have the special property that they remain in the growth phase for a random amount of time and attain, at a population level, a relatively broad distribution of cell sizes. One consequence is that each mother cell can produce a number of daughter cells that is roughly proportional to the logarithm of its size (see **Fig. 2**). Since cell volume is often

considered as a proxy for the cellular metabolic state, the first objective is therefore to develop a model for the cell size distribution under time-independent conditions such as those found in the bioreactor at the MPIMP. The model can be used to calculate and compare stationary distributions for the common binary and the multiple division processes **[9]**.

We have also addressed another set of experiments that were performed in the labs of Prof Martin Steup at the University of Potsdam. In these experiments, the cells are synchronized by fixed periods of light and darkness and are grown in a special medium that does not allow for cell growth in the darkness. Synchronization 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. These experiments allow determining the relationship between the cell size and the number of daughter cells as well as the cell growth rate and the timing of DNA replication. Our current aim is to use our model to predict the cell size distribution at the beginning of the light period.

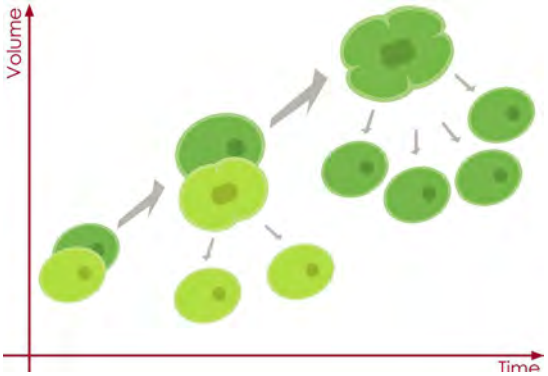

Fig. 2: Multiple cell division. Two twin cells grow in volume over time but one cell divides earlier than the other. The first dividing cell (light green) is relatively small at division time and produces only two daughter cells. The cell that divides later (dark green) attains a larger volume and can divide in four daughter cells. In the cell culture, one can observe also large mother cells producing up to 32 daughter cells.

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Patterns on Complex Networks

In this research activity, we consider networks as collections of points, called vertices, connected by bi-directional links, sometimes also called edges. Random networks are those networks in which the number of edges connected to any randomly chosen vertex, which is called the degree of the vertex, is a random variable that follows a given distribution. This distribution is called the degree distribution of the network. A special subset of these random networks is given by those characterized by a power law degree distribution. Random networks are sometimes called complex networks and all known complex networks have a direct or indirect biological origin. Prominent examples are food webs, as well as social and neural networks.

In general, the vertices of biological networks are dynamic and exhibit various properties or internal degrees of freedom that evolve with time. A proper description of the network is then obtained in terms of dynamical variables that are defined for each vertex of the network. In a neural network, for instance, the vertices represent firing and nonfiring neurons and thus switch between an active and an inactive state depending on the signals that arrive from the neurons connected to them.

In general, the dynamics of each vertex is determined by the local interactions of this vertex with its neighbors. 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. One interesting question concerns the result of the update rule once it is repeated many times over the whole networks. In particular, we would like to estimate the number of attractors of the dynamics. We have found out that the knowledge of the degree distribution alone is not sufficient to provide a general answer. Indeed, it turns out that the degree-degree correlation between the vertices plays a major role.

It is perhaps for this reason that most naturally occurring networks have either positive or negative degree-degree correlation. In both cases, the activity patterns are governed by a large number of attractors. In fact, we have found out that in dissortative scale-free networks the number of attractors exhibits a maximum as a function of network size **[10]**, while in assortative networks the number of attractors steadily increases with network size **[11]**. We have indeed found out that the structure of the network takes a peculiar nested form that depends on whether the degree correlation is positive or negative. This structure can be visualized in terms of partially connected subnetworks or layers of different size whose dynamics can be compared with that of Ising models in different dimensions **[12]**.

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Regulation of Bio-Processes

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Most biological processes are tightly regulated. For example, the genetic information is processed in several steps, transcription, translation, and degradation of mRNA and protein. Each of these steps may be the target of regulatory mechanisms that switch a gene on or off or fine-tune the concentration of its product. Our group is interested in the design principles behind these control mechanisms and the underlying physical constraints, with a focus on bacterial systems. In general, we attempt to use theory as a way to bridge between molecular information and its macroscopic (physiological or evolutionary) context.

Dynamics and Regulation of Transcription

The first step in gene expression is transcription by RNA polymerases (RNAPs) that move along a gene and synthesize an RNA copy of its sequence. The dynamics of this process is a complex interplay of stochastic stepping along the DNA and several types of pauses. One question we are interested in is how this complex dynamics affects transcription under conditions where a gene is transcribed by multiple RNAPs simultaneously. Dense RNAP traffic is typical for the transcription of ribosomal RNA (rRNA) in fast growing bacterial cells, as large ribosome concentrations are needed for the high rate of protein synthesis associated with rapid cell growth. Using lattice models that are related to simple exclusion processes from non-equilibrium statistical physics, we found that backtracking pauses (during which RNAPs slide backwards in a diffusive fashion) are strongly suppressed under these conditions, but that pauses without backtracking may severely limit the transcription rate (**Fig. 1**) **[1]**. Rapidly growing cells therefore need to actively suppress such pauses. In bacteria, this is achieved by the so-called ribosomal antitermination system.

The suppression of backtracking pauses in dense RNAP traffic may also be used in regulatory mechanisms: If pausing is coupled to the termination of transcription, the probability of termination can be modulated by the pause duration and, thus, by the transcription rate **[2]**. As a result, transcription can become very sensitive to changes in the rate of transcription initiation.

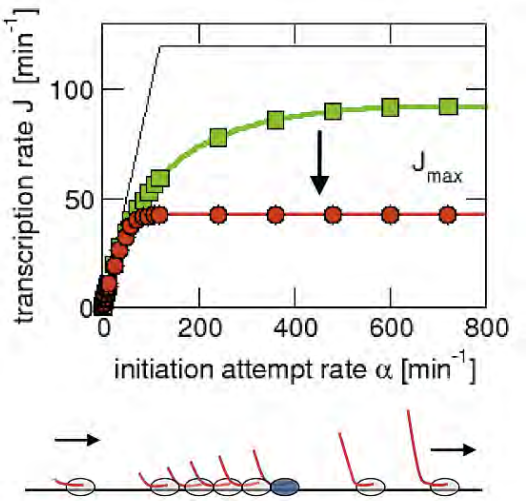

Fig. 1: Pauses during transcription reduce the maximal transcription rate (green to red) due to traffic jams behind paused RNAPs.

Economic Principles of the Transcription and Translation Machinery

RNAPs as well as ribosomes, the molecular machines of translation, are allocated by the cell to genes or classes of genes based on the requirements of their genetic program. For RNAPs, we have used a functional partitioning model (**Fig. 2**) to study this allocation. The model indicates that there is a large pool of RNAPs that are non-specifically bound to DNA. This pool buffers the concentration of free RNAPs against changes in transcription of even highly transcribed genes such as the rRNA genes. Therefore, even dramatic changes in the transcription of a class of gene only weakly affect other genes **[3]**.

Ribosomes underlie different economic principles, as most ribosomes in bacterial cells are active in translation and their activity is directly linked to cell growth. Optimizing ribosome activity therefore provides a fitness advantage, which we have used as a basis to understand the non-random usage of synonymous codons (different nucleotide triplets encoding the same amino acid). An evolution model for codon usage allows us to obtain a prediction of the abundance of a protein from codon frequencies in the sequence of its gene.

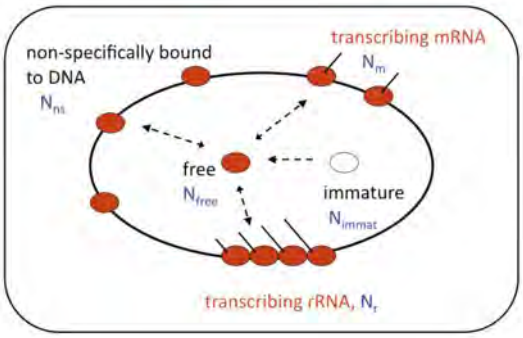

Fig. 2: Model for the partitioning of RNA polymerases into five functional classes.

Genetic Circuits and Growth-Rate Dependent Gene Expression

The control networks of genes regulating other genes are often described in analogy to electrical circuitry. However, genetic circuits remain coupled to the physiological state of their host cell, which for example provides the machinery of gene expression. As a result, the concentration of the product of a gene depends not only on its regulation but also on the state of the whole cell, which in bacteria can often by characterized by the growth rate. We have characterized the growth rate dependence of gene expression of unregulated genes (**Fig. 3**) and several simple circuits **[4]**. If the product of a gene also affects cells growth, these effects can give rise to a new feedback mechanism, mediated by a modulation of cell growth. Such feedback, due to the controlled expression of chromosomal toxins may have a role in the establishment of tolerance against antibiotics (persistence) **[4]**.

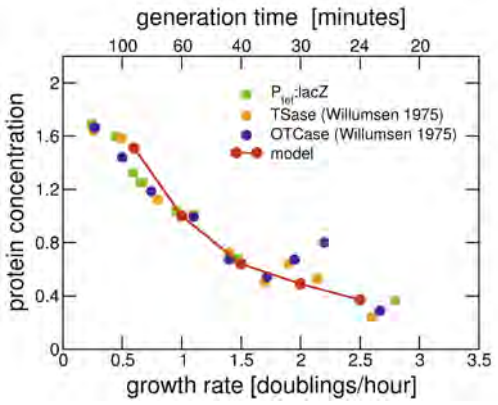

Fig. 3: Growth-rate dependence of gene expression for an unregulated gene, theoretical results (red line) and experimental data for several systems (symbols).

Cooperative Molecular Motors

We have also continued our activity in modeling the cooperative action of small teams of molecular motors. Using detailed simulations of a bead pulled by several kinesin motors **[5]**, we studied how cooperative transport depends on mechanical aspects of the system (collaboration with the group of Ulrich Schwarz, University of Heidelberg). Surprisingly, there is a rather robust relation between the average number of pulling motors and the processivity (run length) of the bead, in good agreement with our earlier model (**Fig. 4**). The increase in processivity with increasing number of motors is also found for motors pulling in opposite directions, despite the tug-of-war between two teams of motors **[6]**.

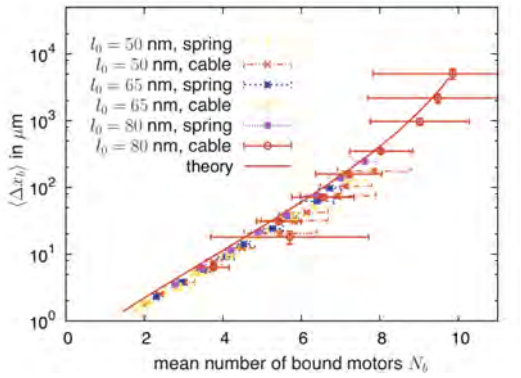

Fig. 4: Run length of a bead transported by several kinesin motors as predicted by simulations that vary the geometrical and mechanical properties of the motors.

S. Klumpp, M. Faber, R. Marathe, M. Mauri, M. Sahoo, P. Patra,
klumpp@mpikg.mpg.de.

References:

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[3] Klumpp, S., Hwa, T.: Growth-rate dependent partitioning of RNA polymerases in bacteria. Proc. Natl. Acad. Sci. USA **105**, 20245-20250 (2008).

[4] Klumpp, S., Zhang, Z., Hwa, T.: Growth-rate dependent global effects on gene expression in bacteria. Cell **139**, 1366-1375 (2009).

[5] Korn, C.B., Klumpp, S., Lipowsky, R., Schwarz, U.S.: Stochastic simulations of cargo transport by processive molecular motors. J. Chem. Phys. **131**, 245107 (2009).

[6] Müller, M.J.I., Klumpp, S., Lipowsky, R.: Bidirectional transport by molecular motors: Enhanced processivity and response to external forces. Biophys. J. **98**, 2610-2618 (2010).

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→ Publications and Patents

APPENDIX

Organigramm
Organization Chart

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Biological Materials

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- Biomimetic Actuation and Tissue Growth/Dr. John Dunlop *(from 2009)*
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- Glycoproteomics/Dr. Daniel Kolarich

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- Polymeric Biomimetics (Emmy Noether Nachwuchsgruppe)/Dr. Laura Hartmann

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- Microreactors as Tools for Organic Chemists/Prof. Peter Seeberger

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- Novel Adjuvants/Prof. Peter Seeberger
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Nanoparticles and Colloidal Polymers

- Nanoparticles and Colloidal Polymers/Prof. Peter Seeberger

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- Electron Microscopic Studies of Colloidal Systems and Biomaterials/Dr. Jürgen Hartmann

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Third Party Funds

Öffentliche Zuwendungsgeber

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
BMBF	Bionik (2): Faserverbundwerkstoffe mit graduellen Matrixübergängen; Teilprojekt 1	Dr. Burgert BM	01.05.2008-30.04.2011	Albert-Ludwigs-Universität Freiburg Universität Bayreuth, Institut für Textil- und Verfahrenstechnik Denkendorf
BMBF	GoFORSYS - Potsdam-Golm BMBF - FORschungs-einrichtung zur SYStembiologie, Photosynthesis and Growth: A Systems Biology-based Approach	Prof. Lipowsky Dr. Valleriani TH	01.06.2006-31.12.2011	MPI für Molekulare Pflanzen-physiologie, Potsdam
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 Gastmolekülen 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	Nachwuchsgruppe Glykobiotechnologie: Malaria-Untersuchung der Erythrozytheninvasion und der schweren Pathologie	Dr. Kamena BS	01.04.2009-31.03.2014	
BMBF	Nachwuchsgruppe Glykobiotechnologie: Funktion der C-Typ Lektinrezeptoren (CLRs) bei der Modulation der	Dr. Lepenies BS	01.02.2009-31.12.2013	Bernhard-Nocht-Institut für Tropenmedizin, Hamburg Universität Regensburg Technische Universität München Universität Würzburg
BMBF	Verbundprojekt:Nanostrukturen zur Lichtinduzier-ten Wasserstoffentwicklung (H_2-NanoSolar)	Prof. Antonietti Dr. Thomas KC	01.09.2009-31.08.2012	Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), Berlin Technische Universität Darmstadt Universität Augsburg Universität Ulm (UU)
BMBF	Verbundvorhaben: Dream Reactions-Stoffliche CO_2-Verwertung	Prof. Antonietti KC	01.03.2009-29.02.2012	Bayer Technology Services GmbH, Leverkusen Technische Universität Dortmund Leibniz-Institut für Katalyse e.V. an der Universität Rostock Forschungszentrum Karslruhe GmbH Rheinisch-Westfälische Technische Hochschule Aachen Technische Universität Darmstadt

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BS – Abteilung Biomolekulare Systeme/Department of Biomolecular Systems
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KC – Abteilung Kolloidchemie/Department of Colloid Chemistry
TH – Abteilung Theorie & Bio-Systeme/Department of Theory & Bio-Systems

BMBF

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
BMBF	Verbundprojekt: Spitzenforschung und Innovation in den neuen Ländern-Das Taschentuchlabor: Impulszentrum für Integrierte Bioanalyse (IZIB)	Prof. Seeberger BS	01.10.2009-30.09.2014	Fraunhofer-Gesellschaft zur Förde - rung der angewandten Forschung e.V. (FhG), München Universität Potsdam Charitè-Universitätsmedizin Berlin Helmholtz-Zentrum für Infektions-forschung GmbH, Braunschweig Ruhr-Universität Bochum IDM Institut für Dünnschichttechno-logie und Mikrosensorik e.V., Teltow Technische Fachhochschule Wildau MicroDiscovery GmbH, Berlin BST Bio Sensor Technologie GmbH, Berlin Congen Biotechnologie GmbH, Berlin Scienion AG, Dortmund Poly-An Gesellschaft zur Herstel-lung von Polymeren für spezielle Anwendungen und Analytik mbH, Berlin
BMBF	Fortführung der experimentellen und theoretischen Untersuchung zur Bildung und Deformation von Einzeltropfen als Modell für Schäume und Emul-sionen sowie Begleitung der FASES-Experimente auf der ISS	Dr. Miller GF	01.07.2009-30.06.2011	IENI, Genua, Italien Université Aix-Marseille Université Compiegne, France Universität Complutense Madrid Universität Florenz IPF, Dresden Aristotele Universität Thessaloniki
BMBF	Verbundprojekt: Spitzenforschung und Innovationen in den neuen Ländern-Light2Hydrogen - Energie für die Zukunft - Photokatalytische Spaltung von Wasser zu Wasserstoff -TP2	Prof. Antonietti KC	01.11.2009-31.10.2014	Leibniz-Institut für Katalyse e.V. an der Universität Rostock Leibniz-Institut für Plasmaforschung und Technologie e.V. (INP), Greifswald Technische Universität Berlin Helmholtz-Zentrum Berlin für Mate-rialien und Energie GmbH (HZB), Berlin Fachhochschule Stralsund Universität Rostock
BMBF	Planare Nanostrukturen an festen Oberflächen	Prof. Vollhardt GF	01.07.2007-31.12.2009	National Academy of Sciences of Ukraine
A.v.H.	Max-Planck-Forschungspreis 2008: Biological and Biomimetic Materials	Prof. Fratzl BM	01.09.2008-31.08.2013	Ludwig Boltzmann Institute of Osteology, Vienna, Austria Harvard University, Department of Chemistry and Chemical Biology, USA University of California at Santa Barbara, USA Weizmann Institute of Science, Rehovot, Israel Montanuniversität Leoben, Austria Institut National Polytechnique de Grenoble, France Department of Materials Science, Technion, Haifa, Israel

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Zuwendungs - geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
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
BMBF	ForMaT: Potenzial-Screening durch ein Konzeptteam und Entwicklung eines Konzeptes zur Vermarktung intelligenter Nanobehälter für selbstheilende Antikorrosionsbeschichtungen	Dr. Shchukin GF	01.10.2009-31.03.2010	EADS Deutschland GmbH, München Volkswagen AG, Wolfsburg Mankiewicz Gebr & Co. (GmbH & Co. KG), Hamburg BASF Coatings AG, Münster Chemetall GmbH, Frankfurt am Main Lankwitzer Lackfabrik GmbH, Berlin
BMBF	Verbundprojekt: Molekulare Pathologie der Osteoporose (OsteoPath)	Prof. Fratzl Dr. Wagermaier BM	01.06.2010-31.05.2013	Ludwig Boltzmann Gesellschaft, Ludwig Boltzmann Institut für Osteologie, Wien
BMBF	ForMaT	Dr. Shchukin GF	01.12.2010-30.11.2012	EADS Deutschland GmbH, München Volkswagen AG, Wolfsburg Mankiewicz Gebr & Co. (GmbH & Co. KG), Hamburg BASF Coatings AG, Münster Chemetall GmbH, Frankfurt am Main Lankwitzer Lackfabrik GmbH, Berlin Ludwig Boltzmann Gesellschaft, Ludwig Boltzmann Institut für Osteologie , Wien

Länder

MWFK / LASA Brandenburg GmbH	Verbundforschung Biokohle Brandenburg- Herstellung und Verwendung von Biokohle aus hydrothermaler Karbonisierung	Prof. Antonietti KC	01.02.2009-05.12.2011	Fachhochschule Eberswalde

EU

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

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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	Bio-imaging with Smart Functional Nanoparticles (BONSAI)	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	Development a new biocoatinng-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; ParisFutureCarbon 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 (MUST)	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 fizykochemii Powierzchni, Polska Akademia Nauk, Krakau; Steinbeis Advanced Risk Technologies 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 Multifunctional Materials AISBL, Belgien

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Zuwendungs - geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
EU	Carbohydrate Multivalent Systems as tools to study Pathogen interaction with DC-Sign (Carmusys)	Prof. Seeberger BS	01.01.2009-31.12.2012	Agencia Estatal Consejo Superior De Investigaciones Cientifícas (CSIC), Spain; Universita Degli Studi Di Milano (UNIMI), Italy; Centre National De La Recherche Scientifique (CNRS), France; Fundación Para La Investigación Biomédica del Hospital Universitario "Doce de Octubre", Spain; The Chancellor, Masters and Scholars of the University of Oxford, United Kingdom; Vysoka Skola Chemicko-Technologicka V Praze, Czech Republic; Vereniging Voor Christelijk Hoger Onderwijs Wetenschappelijk Onderzoek En Patientenzorg, Netherlands; Anterio Consult & research GmbH, Germany; DC4U, Netherlands; Institut National De La Sante Et De La Recherche Medicale, France; Vrije Universiteit Medisch Centrum, Niederlande; Universite Joseph Fourier Groble, Frankreich
EU	Vesicle formation driven by ESCRT (endosomal sorting complex required fro Transport) (vesicle ESCoRT)	Dr. Valleriani TH	15.10.2009-14.09.2012	National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Helth, USA
EU	Development of carbohydrate array technology to systematically explore the functional role of glycans in helthy and diseased states (EuroGlycoArrays)	Prof. Seeberger BS	01.09.2008-31.08.2012	The University of Manchester, United Kingdom; Centre National de la Recherche Scientifique, Paris, France; Universität für Bodenkultur Wien, Austria; Eidgenössische Technische Hochschule Zürich, Switzerland; The University of Reading, United Kingdom; Deutsches Krebsforschungszentrum, Heidelberg, Germany; Stockholms Universitet, Sweden; Centre for Cooperative Research in Biomaterials -CIC biomaGUNE, San Sebastian, Spain; Universität Bayreuth, Germany; Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry, Moscow, Russia; Imperial College of Science, Technology and Medicine, London, United Kingdom; University of Zagreb, Kroatien; University of Copenhagen, Denmark; GALAB Laboratories GmbH, Geesthacht, Germany; Ludger Ltd., Abingdon, United Kingdom; National Institute for Bioprocessing Research and Training Ltd., Dublin, Ireland

EU

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
EU	Hydrothermal and Ionothermal Chemistry for Sustainable Materials	Prof. Antonietti KC	01.11.2008-31.10.2013	
EU	Automated Synthesis of Heparin and Chondroitin Libraries for the Preparation of Diverse Carbohydrate Arrays	Prof. Seeberger BS	01.01.2009-31.12.2013	

DFG

DFG	Mesoskopisch strukturierte Verbundsysteme; Wandverformung bei Mesoporen bei der Kappilarkondensation von Fluiden	Prof. Fratzl Dr. Paris BM	01.01.2007-31.12.2009	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam
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. Inderchand BM	01.01.2007-31.12.2010	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	01.01.2007-31.12.2010	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	01.01.2007-31.12.2010	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	Mesoskopisch strukturierte Verbundsysteme; Hierarchische Architekturen aus Modulen mit metallosupramolekularen Koordinations-Polyelektrolyten	Prof. Möhwald Dr. Kurth GF	01.01.2001-31.12.2009	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam

DFG

Zuwendungs - geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Mesoskopisch strukturierte Verbundsysteme; Ordnungsstrukturen in Systemen aus stäbchenförmigen Molekülen	Prof. Lipowsky TH	01.01.2004-31.12.2009	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam
DFG	Mesoskopisch strukturierte Verbundsysteme; Molekulare Prozesse in mesoskopisch srukturierten Polyelektrolytsystemen	Prof. Möhwald GF	01.01.2004-31.12.2009	Humboldt-Universität Berlin Freie Universität Berlin Technische Universität Berlin Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam
DFG	Fluide Grenzflächen	Dr. Miller IF	01.05.2010-30.04.2013	
DFG	Förderung des Gastaufenthaltes von Dr. Salah A-Thyabat, Al-Hussein Bin Talal University, Ma'an, Jordanien	Dr. Miller IF	10.06.-12.08.2010	Al-Hussein Bin Talal University, Ma'an, Jordanien
DFG	Synthesis and properties of glycopolypeptide biohybrid materials Theme: Novel Polymer Synthesis and New Supramolecular Polymer Assemblies	Dr. Schlaad KC	20.10.2010	
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	01.01.2007-31.01.2010	
DFG	Materials World Network to study liquid Precursor Formation and Crystallization at Interfaces: Fundamentals towards Applications	Dr. Cölfen KC	01.01.2008-31.05.2010	
DFG	Charakterisierung von Grenzflächen zwischen zwei Flüssigkeiten unter hoch-dynamischen Bedingungen	Dr. Miller IF	01.08.2009-31.07.2011	
DFG	Charakterisierung von Grenzflächen zwischen zwei Flüssigkeiten unter hoch-dynamischen Bedingungen	Dr. Miller GF	01.08.2007-31.07.2009	
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	01.01.2008-31.08.2010	
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	01.12.2007-30.11.2009	
DFG	Structural and morphological characterization of ceramide-1-phoshate model membran	Dr. Brezesinski GF	20.09.2007-31.10.2012	

DFG

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Dynamics of Interfaces between Drops with Miscible Liquids	Dr. Riegler GF	01.09.2008-31.08.2011	
DFG	Intelligent release systems for anticorrosion self-healing coatings (Deutsch-Russisches Kooperationsprojekt)	Prof. Möhwald GF	17.07.2008-16.07.2011	Dr. V.V. Volkov, Shubnikov Institute of Crystallography, RAN, Moscow
DFG	Generation of nanoparticels with tunable surface wettability and surface functionality to cross hydro-phlilic/hydrophobic interfaces of biological barriers	Prof. Möhwald Dr. Wang GF	01.07.2009-30.06.2011	
DFG	N-heterocyclic carbenes incorporated in porous networks	Dr. Thomas KC	02.03.2009-30.11.2009	Projektübertragung an TU-Berlin 12/2009, da Weggang Wissen-schaftler und Projektmitnahme
DFG	Thermodynamisch stabile Pickering-Emulsionen	Dr. Wüstneck GF	01.09.2009-31.08.2011	
DFG	Biometric Materials Research: Functionality by Hierarchical Structuring of Materials	Prof. Fratzl Dr. Aichmayer Dr. Zaslansky Dr. Faivre Dr. Burgert Dr. Schlaad Dr. Cölfen BM	01.05.2010-	(MPI KOLL ist Koordinator, 7 Teilprojekte am Institut) Institut National Polytechnique; E.N.S.E.E.G./ L.T.P.C.M. Grenoble Foundry Institute of RWTH Aachen Department of Materials Engineering, Technical University Berlin Evolutionary Biomaterials Group, MPI für Metallforschung, Stuttgart Department of Materials Science and Engineering, University Erlangen-Nürnberg Dept. Of Microstructure Physics and Metal Forming, MPI Eisenforschung Düsseldorf Plant Biomechanics Group, Botanic Garden, University of Freiburg
DFG	Emmy-Noether-Programm	Dr. Hartmann BS	04.08.2009-03.07.2012	
DFG	Gottfried Wilhelm Leibniz-Programm	Prof. Fratzl Dr. Dunlop Dr. Wagermaier BM	01.09.2010-31.08.2017 01.09.2010-31.12.2011 01.01.2011-31.12.2012	2 Subprojekte am Institut
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 bio-mimetische Polymere zur programmierbaren Struk - turierung synthetischer Polymermaterialien: Syn - these, Charakterisierung und Anwendung der Polymerhybridsysteme	Dr. Börner KC	01.04.2005-31.03.2009	

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
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
FU Berlin	Initiative: CSI-Center for Supramolecular Interactions	Dr. Hartmann BS	01.01.2010	Freie Universität Berlin
OOO 'Delta XXI Vek', Saratov	Training in nanotechnology and material science (interface phenomena)	Prof. Brezesinski GF	01.10.2010-31.12.2011	Universität Saratov, Russland

Supranationale Einrichtungen

ESA/ESTEC	FASES - Fundamental and applied studies of emulsion stability	Dr. Miller GF	01.10.2003-31.07.2013	IENI, Genua, Italien Université Aix-Marseille Université Compiegne, France Universität Complutense Madrid Universität Florenz; IPF, Dresden CNR - Consiglio Nazionale delle Ricerche, Italien; Eni S.p.A., Italien Aristotele Universität Thessaloniki
ESA/ESTEC	Topical Team: Foam and Emulsion Technologies-Concerted Action Team (FETCAT)	Dr. Miller GF	01.10.2003-30.12.2011	CNR, Genua, Italien Universität Florence, Italien Universität Marseille, Frankreich Universität Compienge, Frankreich Murmansk State Technical Univer-sity, Russland; Aristotele Uni - versität Thessaloniki, Griechenland Universität Stockholm, Schweden EniTecnologie, Milano, Italien University College Dublin, Irland Nestlé Research Center, Lausanne, Schweiz; Wageningen University, Niederlande; University of Manchester Institute of Science and Technology, Großbritanien Institute of Food Research, Norwich, Großbritanien; Norwegian Univerity of Science and Technology, Trondheim, Norwegen St. Petersburg State Univerity, Russland; Université d'Orsay et CNRS, Frankreich; Université de Marne La Vallée, Frankreich Unilever, Großbritanien Norsk Hydro ASA, Norwegen IPF, Dresden
NATO	Nato-Collobarotive Linkage Grant, as coordinator, for the project "Smart Textile Materials with In-herent Remote Identification Ability"	Prof. Möhwald Dr. Shchukin GF	29.06.2009-28.06.2011	St. Petersburg State University of Technology, Russland

Stiftungen

Zuwendungs-geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
Körber-Stiftung	Körber-Preis 2007	Prof. Seeberger BS	01.01.09.2007-	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, Braunschweig
GIF-German Israeli Foundation	Gene manipulation of amorphous biomineralogy	Dr. Aichmayer BM	01.01.2009-31.12.2011	Ben Gurion University, Israel

Ausländische Forschungsfinanzierer

Forsyth Institute	Matrix Protein Regulation of Enamel Formation	Prof. Fratzl BM	01.08.2005-31.07.2009	The Forsyth Institute, USA
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	Japan Science and Technology Agency, Japan
Schweizer Nationalfonds	Probing Hierarchical Self-Assemblies	Prof. Seeberger BS	01.03.2009-28.02.2010	
Schweizer Nationalfonds	Automated solid-phase synthesis of oligosaccharides	Prof. Seeberger BS	01.01.2009-30.09.2010	
Schweizer Nationalfonds	The Role of Glycosylphosphatidylinositol Oligosaccharides in Malaria	Prof. Seeberger BS	01.01.2009-30.05.2011	
Schweiz. Eid - genossenschaft (BABS - Labor Spies)	Entwicklung von Antikörpern gegen Yersinia pestis	Prof. Seeberger BS	01.01.2009-31.12.2010	
Schweiz. Eid-genossenschaft (Labor Spiez)	Impact of microreactors on the Chemical Weapons Convention's Chemistry-Screening of some basis key-reactions	Prof. Seeberger BS	01.01.2010-31.03.2011	

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	Nanoskalige Hohlstrukturen mit eingebetteten Gastmolekülen	Prof. Möhwald Dr. Shchukin GF	01.02.2007-30.09.2009	
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	

Industrie

Zuwendungs - geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
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	
BASF	Nanoskalige Systeme als Haftvermittler konzipieren und in Lacken einsetzen	Prof. Möhwald Dr. Wang GF	01.01.2009-31.12.2010	
BASF	Modification of the CSH assemblage by polymers	Dr. Cölfen KC	01.09.2009-31.07.2010	Vertrag ab 01.08.2010 an Uni Konstanz
Merck	CASE Studentship Agreement	Prof. Seeberger BS	01.01.2009-15.12.2010	
Beiersdorf AG	Glycomics der Haut	Prof. Seeberger BS	01.12.2009-31.01.2011	
AstraZeneca UK Unlimeted	Synthetic Organic Chemistry in Continuous Flow	Prof. Seeberger BS	01.12.2009-30.11.2011	
Merck	HPLC-Collaboration Agreement	Prof. Seeberger BS	07.10.2010-06.10.2011	

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	01.01.1999-20.06.2010	HMI Berlin
DAAD	Projektbezogener Personenaustausch mit der VR-China - PPP VR China	Dr. Shchukin GF	2009 und 2010	Jilin Univerity, VR China
DAAD	Projektbezogener Personenaustausch mit Frankreich (PROCOPE)	Dr. Dimova TH	2009 und 2010	Institut de Chimie Seprative de Marcoule, Frankreich

Ausgewählte Veranstaltungen
Selected Events

- **12. March 2009 SchülerCampus Brandenburg**
  Martin Haase: Wie Nanoteilchen Metalle vor Rost schützen
  Dr. Volker Knecht: Auf die Faltung kommt es an - Molekulare Grundlagen von Alzheimer und Rinderwahn

- **12. May 2009 Workshop: "Bioactive Surfaces - From fundamental understanding to Life Science applications"**
  Potsdam-Golm Science Park

- **1.-3. June 2009 Max Planck Summer School on Amorphous Solids in Physics and Biology**
  Schloss Neuhardenberg

- **3.-5. June 2009 4th International Workshop on Vibrational Spectroscopy of Thin Films (VSM4)**
  MPI of Colloids and Interfaces

- **12. June 2009 Alumni Meeting Trends in Colloids and Interfaces Science**
  MPI of Colloids and Interfaces

- **8. September 2009 Open Day at the Research Campus Potsdam-Golm**
  Max-Planck-Campus

- **6. October 2009 Fact-Finding-Tour of Indian Journalists**
  MPI of Colloids and Interfaces, Max Planck Institute for Gravitational Physics (Albert Einstein Institute)

- **3. November 2009 Besuch des Landesarbeitskreis „Innovative Technologien" (Unternehmerverband Brandenburg e.V.)**
  MPI of Colloids and Interfaces

- **10.-12. February 2010 Meeting of the Scientific Advisory Board**
  MPI of Colloids and Interfaces

- **23.-26. March 2010 SPP 1420 DFG Priority program – Biennial Winter School 2010**
  Kerkrade, Niederlande

- **19. April 2010 "Royal Visit": The Thai princess, Her Royal Highness Chulabhorn Mahidol, is visiting the department of Biomolecular Systems at the Max Planck Institute of Colloids and Interfaces**
  MPI of Colloids and Interfaces, Department of Biomolecular Systems at the FU Berlin-Dahlem

- **22. April 2010 Girl's Day at the Max Planck Institutes for Gravitational Physics (Albert Einstein Institute) and of Colloids and Interfaces**
  Potsdam-Golm Science Park

- **18. May 2010 Launch of the floating science centre MS Wissenschaft**
  Exhibit „Green coal" of the MPI of Colloids and Interfaces Berlin-Spandau, Germany

- **23. May 2010 100 Jahre nach Robert Koch: Tropenkrankheiten und das Immunsystem – Dr. Bernd Lepenies**
  Sunday Lecture in the The House of Brandenburg-Prussian History Potsdam

- **4. June 2010 Alumni Meeting**
  MPI of Colloids and Interfaces

- **10. August 2010 20 Jahre Land Brandenburg - Strukturwandel, Stadtentwicklung und Wissenschaftslandschaft**
  Visit of the Brandenburg Minister for Science, Research and Culture Martina Münch and West German science journalists

- **25. September 2010 Energy Day 2010**
  Potsdam-Golm Science Park

- **27. October 2010 „Wissenschaft vor Ort": The Max Planck Institute of Colloids and Interfaces introduces itself**
  MPI of Colloids and Interfaces, Department of Biomolecular Systems at the FU Berlin-Dahlem

Wissenschaftliche Abschlüsse
Scientific Degrees

Diploma Theses

Department of Biomolecular Systems:

Suna, Gonca: Cloning and Expression of the C-type lectin receptor CLEC6A (dectin-2). Medizinische Universität Innsbruck (2010).

Wehler, Patrizia: Entwicklung einer neuen Methode zur in vitro Produktion von glykosylierten Proteinen. Freie Universität Berlin (2010).

Ecker, Melanie: Sequenzspezifische Einführung von anionischen Gruppen in linearen, monodispersen Poly(amidoaminen). Freie Universität Berlin (2010).

Department of Colloid Chemistry:

Werner, Mayke: Synthese und Charakterisierung von optisch-aktiven mikroporösen Poymeren. Universität Potsdam (2010).

Master Theses

Department of Biomolecular Systems:

Stanslowsky, Nancy: Identifizierung peptidischer Kohlenhydratmimotope mittels Phagen-Display am Beispiel von Heparansulfat-Proteoglykanen. Biotechnology Degree Program the Beuth Hochschule für Technik Berlin – University of Applied Sciences (2010).

Ponader, Daniela: Synthesis of Novel Functional Building Blocks for Sequence-Defined Solid Phase Synthesis of Neoglycopolymers. Freie Universität Berlin (2010).

Hart, Felix: Investigation of the Role of Lectin–Glycan Interactions during Host Cell Invasion by Apicomplexan Parasites Using Surface Plasmon Resonance. Biotechnology Degree Program the Beuth Hochschule für Technik Berlin – University of Applied Sciences (2010).

Pussak, Daniel: Synthesis and Functionalization of Poly(ethylene glycol) Microparticles for Biosensing. Freie Universität Berlin (2010).

Horstmann, Benjamin: Synthesis of Mannose bearing Building Blocks for the Poly(amidoamine) Solid Phase Synthesis. Freie Universität Berlin (2010).

PhD Theses

Department of Biomaterials:

Goswami, Luna: Enzymatic modification of wood cell walls and its influence on material properties and function. Humboldt-Universität Berlin (2009).

Liu, Yifei: The micro-mechanical and structural properties of callus tissue during bone healing. Humboldt-Universität Berlin (2010).

Müter, Dirk: Sorption von Fluiden in mesoporösen Silikamertialien: Modellierung des Sorptionsverhaltens und elastischer Verformungen. Humboldt-Universität Berlin (2010).

Seto, Jong: On the multiscale, mechanical behaviors of mineralized bones. Technische Universität Berlin (2010).

Department of Biomolecular Systems:

Kröck, Lenz: A New Linker and a New Synthesis Instrument as Key to the Automated Synthesis of Complex Oligosaccharides. ETH Zurich (2009).

Castelli, Riccardo: New Tools for the Total Synthesis of Glycosylphosphatidylinositol Anchor Glycans. ETH Zurich (2009).

Oberli, Matthias: Synthesis of Cell Surface Carbohydrate Antigens. ETH Zurich (2009).

Horlacher, Tim: Analysis of Protein Interactions, Biological Functions and Immunogenicity of Carbohydrates Using Synthetic Oligosaccharides. ETH Zurich (2009).

Hecht, Marie-Lyn: Structure-Activity Relationships of Complex Carbohydrates. ETH Zurich (2010).

Stallforth, Pierre: Synthesis of Bacterial Carbohydrates and Glycolipids for Application in Novel Vaccine Strategies. ETH Zurich (2010).

Department of Interfaces:

Blacklock, Jenifer: Self-Assembly of Thin Films for Localized Delivery Systems. Wayne State University (2009).

Bèdard, Mattieu: Light Addressable Capsules. Queen Mary, University of London (2009).

Dönch, Ingo: Mechanische Eigenschaften von Polyelektrolyt-Multilagen bei verschiedenen Ladungsdichten und Hydrationszuständen. Universität Potsdam (2009).

Kotsmar, Csaba: Structure and Dynamics of Mixed Milk Protein/Surfactant Interfacial Layers. Universität Potsdam (2009).

Radziuk, Darya: Ultrasonic activation of nanocatalysts and formation of binary nanoparticles. Universität Potsdam (2009).

Saraiva, Ana: Interaction Studies between Biocompatible Polymers and Amyloid-β Peptides. University of Porto (2009).

Schmidt, Stephan: Motility and Force Generation Based on the Dynamics of Actin Gels. Universität Bayreuth (2009).

Vergin, Annika: Charakterisierung von Metallosupramolekularen Polyelektrolyten mittels Analytischer Ultrazentrifugation. Universität Potsdam (2009).

Bai, Shuo: Active Hydrogels with Nanocomposites. Universität Potsdam (2010).

Belova, Valentina: Composite Fabrication and Surface Modification via High Intensity Ultrasound. Universität Potsdam (2010).

Chanana, Munish: Stimuli-Responsive Inorganic Nanoparticles for Bio-Medical Applications. Universität Potsdam (2010).

Radziuk, Darya: Ultrasonic Activation of Nanocatalyts and Formation of Binary Nanoparticles Universität Potsdam (2010).

Sievers, Torsten: Tuning and Understanding Chain-Length of Metallo-Supramolecular Coordination Polymers. Universität Potsdam (2010).

Stöckle, Silke: Thin Liquid Films with Nanoparticles and Rod-like Ions as Models for Nanofluidics. Universität Potsdam (2010).

Travkova, Oksana: Interactions of Antimicrobial Peptide Arenicin with Amphiphiles at Planar and Curved Surfaces. Universität Potsdam (2010).

Department of Colloid Chemistry:

Bojdys, Michael Janus: Über neue Allotrope und Nanostrukturen von Karbonitriden. Universität Potsdam (2009).

Demir-Cakan, Rezan: Synthesis, characterization and applications of nanostructured materials using hydrothermal carbonization. Universität Potsdam (2009).

Diehl, Christina: Functional microspheres through crystallization of thermoresponsive poly(2-oxazoline)s. Universität Potsdam (2009).

Hahn, Harald: Modularer Ansatz zu multifunktionellen Polymer-Peptid-Fasern. Universität Potsdam (2009).

Karabudak, Engin: Development of MWL-AUC/CCD-C-AUC/SLS-AUC detectors for the analytical ultracentrifuge. Universität Potsdam (2009).

Lausser, Christine: Synthese und Charakterisierung funktionaler Mesokristalle. Universität Potsdam (2009).

Makowski, Philippe Denis: From supported palladium to metal free catalyts: different approaches in heterogeneous catalysis. Universität Potsdam (2009).

Paraknowitsch, Jens Peter: Entwicklung von Kohlenstoffmaterialien für Energieanwendungen durch gezielte Modifikation der chemischen Struktur. Universität Potsdam (2009).

Roohi, Farnoosh: Synthesis and evaluation of thermo-responsive stationary phases for high performance liquid chromatography (HPLC). Universität Potsdam (2009).

Gentsch, Rafael: Complex bioactive fiber systems by means of electrospinning. Universität Potsdam (2010).

Hermes, Florian: Polypeptide-Hybrid Block Copolymers: Chain Length and Conformation Effects on the Self-Assembly in Solution. Universität Potsdam (2010).

Ritter, Nicola: Microporous high performance polymers; The Limits of Intrinsic Microporosity. Universität Potsdam (2010).

Schmidt, Johannes: Templatfreie Synthese funktionaler mikroporöser Polymernetzwerke. Universität Potsdam (2010).

Verch, Andreas: Pränukleationscluster und ihre Wechselwirkungen mit Additiven. Universität Potsdam (2010).

Zhao, Li: Sustainable Approaches towards Novel Nitrogen-Doped Carbonaceous Structures. Universität Potsdam (2010).

Department of Theory & Bio-Systems

Baczynski, Krzysztof Konrad: Buckling instabilities of semiflexible filaments in biological systems. Universität Potsdam (2009).

Li, Yanhong: Phase separation in giant vesicles. Universität Potsdam (2009).

Knorr, Roland: Giant vesicles – influence of phase state, composition and electric pulses. Universität Potsdam (2010).

Menche, Jörg: Aktivitätsmuster auf Netzwerken. Universität Potsdam (2010).

Personalien
Appointments and Honors

2009

Ehrungen/Mitgliedschaften/Honorarprofessuren

Honors/Memberships/Honorary Professorships

Prof. Dr. Markus Antonietti	Director of the Department of Colloid Chemistry is laureate of The Macro Group UK Medal for Outstanding Achievement 2008.
Prof. Dr. Peter Fratzl	Director of the Department of Biomaterials received the Leibniz Prize
Prof. Dr. Peter Fratzl	Director of the Department of Biomaterials became supervisory board member of the Helmholtz-Zentrum Berlin für Materialien und Energie GmbH
Prof. Dr. Helmuth Möhwald	Director of the Department of Interfaces obtained the Wolfgang Ostwald Prize for scientific life-time achievement.
Prof. Dr. Peter H. Seeberger	Director of the Department of Biomolecular Systems obtained the Tetrahedron Young Investigator Award 2010 for Bioorganic and Medical Chemistry
Prof. Dr. Peter H. Seeberger	Director of the Department of Biomolecular Systems obtained the Claude S. Hudson Award of the American Chemical Society in Carbohydrate Chemistry
Dr. Margarita Staykova	Member of the Department of Theory & Bio-Systems obtained the "Women in Science" Award

2010

Prof. Abdel Salam Hamdy Makhlouf	Member of the Department of Interfaces and recipient of the Alexander von Humboldt Experienced Researchers Program has been awarded the Prize of Excellence and Innovation in Materials Science and their Applications. Egypt, 2010.
Dr. Maria-Magdalena Titirici:	Group Leader in the Department of Colloid Chemistry has been awarded the 15th Desty Memorial award for Innovation in Separation Science. This honour is associated with the 15th Desty Memorial Lecture for Innovation in Separation Science, which will take place in the Royal Institution of Great Britain London on Wednesday 6th October 2010.
René Genz:	Apprentice in the IT-group received one of the apprentice prizes 2010 from the Max Planck Society.

2009

Ruf an eine Universität

Appointments

Prof. Dr. Peter Fratzl	Director of the Department of Biomaterials accepted a position as Honorary Professor (Physics of Biomaterials) at the University of Potsdam.
Dr. habil. Arne Thomas	Group Leader in the Department of Colloid Chemistry accepted a position as professor (W3) for Functional Materials at the Technical University Berlin.
Dr. habil. Hans Börner	Group Leader in the Department of Colloid Chemistry accepted a position as professor (W3) for Organic Chemistry of Functional Systems at the Humboldt University of Berlin.

2010

Dr. habil. Helmut Cölfen	Group Leader in the Department of Colloid Chemistry accepted a position as professor (W3) for Physical Chemistry at University Konstanz
Dr. Inderchand Manjubala	Group Leader in the Department of Biomaterials accepted a position as Professor at the Biomedical Engineering Division, School of Bio Sciences and Technology, VIT University Vellore, Tamilnadu, India
Dr. Takashi Nakanishi	Group Leader in the Department of Interfaces accepted a position as Principal Researcher for Organic Nanomaterials at the National Institute for Materials Science (NIMS) Tsukuba, Japan
Dr. Dayang Wang	Group Leader in the Department of Interfaces accepted a position as Research Professor for Physical Chemistry at the Ian Wark Research Institute, University of South Australia

Wissenschaftliche Veröffentlichungen
Publications

Biomaterials 2009

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