

**Max Planck Institute of Colloids and Interfaces**

# BIANNUAL REPORT 2001-2002



MAX-PLANCK-GESELLSCHAFT



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of Colloids and Interfaces**

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# INHALTSVERZEICHNIS

## TABLE OF CONTENTS

<b>Vorwort</b>	6
<b>Preface</b>	7
Prof. M. Antonietti	
<b>Rückschau – Die ersten elf Jahre</b>	8
<b>Looking Back – The First Eleven Years</b>	9
Prof. H. Möhwald	
<b>Das Forschungsprogramm des Max-Planck-Institutes für Kolloid- und Grenzflächenforschung</b>	10
<b>The Research Program of the Max Planck Institute of Colloids and Interfaces</b>	13
Prof. R. Lipowsky	
<b>Wissenschaftliche Beziehungen</b>	16
<b>Scientific Relations</b>	17
<b>International Max Planck Research School (IMPRS) on Biomimetic Systems</b>	18
Dr. A. Valleriani	
<b>Öffentlichkeitsarbeit</b>	22
<b>Public Relations</b>	23
Katja Schulze	
<b>COLLOID CHEMISTRY</b>	
Research in the Department of Colloid Chemistry · Prof. M. Antonietti	26
<b>Heterophase Polymerization</b>	
Miniemulsions · Dr. K. Landfester	28
Heterophase Polymerization · Dr. K. Tauer	30
<b>Polyelectrolytes and their Complexes</b>	
Ionic Self-Assembly: Facile Route for the Production of Functional Nanostructured Materials · Dr. C. Faul	32
<b>Amphiphilic Polymers</b>	
Bioorganic - Synthetic Hybrid Polymers as Molecular LEGO® - Bricks · Dr. H. Börner	34
Biomimetic Mineralization · Dr. H. Cölfen	36
Amphiphilic Block Copolymers · Dr. H. Schlaad	38
<b>Mesoporous Materials by Nanocasting and Nanocoating</b>	
Porous Materials via Nanocasting Procedures: Innovative Materials and Learning about Softmatter Organization · Prof. M. Antonietti	40
Templating Strategies to Fabricate Controlled Morphology Networks · Dr. R. A. Caruso	42
<b>Modern Techniques of Colloid Analysis</b>	
Fractionating Colloid Analysis · Dr. H. Cölfen	44
Electron Microscopic Studies of Colloidal Systems · Dr. J. Hartmann	46
Gel Permeation Chromatography (GPC), Static Light Scattering (SLS) · Dr. G. Rother	48
Modern Methods of Light Scattering · Dr. R. Sigel	50
<b>Independent Research Group Surfactant Adsorption Layers</b>	
Adsorption Properties of Surfactants at Fluid and Solid Interfaces · Dr. K. Lunkenheimer	52

<b>INTERFACES</b>	
Research in the Department of Interfaces · Prof. H. Möhwald	56
<b>(Quasi) Planar Interfaces - Fluid Interfaces</b>	
Interactions in Complex Monolayers · Dr. G. Brezesinski	58
Analysis – Synthesis – Purification of Amphiphiles · Dr. G. Czichocki	60
Static and Dynamic Peculiarities of Two Dimensional Systems (Langmuir Monolayers) · Dr. T. Fischer	62
Thermodynamics, Kinetics and Dilational Rheology of Interfacial Layers · Dr. R. Miller	64
Molecular Organization in Soluble Monolayers and Functional Films · Dr. H. Motschmann	66
Thin Liquid Films · Dr. H.-J. Müller	68
Supramolecular Organization of Amphiphilic Monolayers · Prof. D. Vollhardt	70
Rheological Properties of Fluid Interfaces · Dr. K.-D. Wantke	72
<b>Non-Planar Interfaces</b>	
Nanostructured Interfaces and Materials · Prof. F. Caruso	74
Mechanics and Adhesion of Capsules and Strongly Deformable Colloids · Dr. A. Fery	76
Modular Materials: From Dynamic to Nanotechnological Devices · Dr. D. G. Kurth	78
Bioinspired Control of Electrical and Optical Properties of Interfaces · Prof. H. Möhwald	80
Dynamics of Complex Polymer Layers · Dr. M. Schönhoff	82
Multifunctional Polymeric Micro- and Nanosized Capsules · Dr. G. Sukhorukov	84
<b>Solid Interfaces</b>	
Nucleation, Interfacial Molecular Ordering and Wetting Behavior of Alkanes at Solid/Vapor Interfaces · Dr. H. Riegler	86
<b>International Joint Laboratory</b>	
Assembly of Complex and Biomimetic Materials · Prof. J. Li	88
<b>Research Group Nanotechnology for Life Science</b>	
A Cooperation between the MPI of Colloids and Interfaces and the Fraunhofer Institute for Applied Polymer Research · Dr. A. Thünemann	90
<b>THEORY</b>	
Research in the Theory Department · Prof. R. Lipowsky	94
Wetting Phenomena at Structured Surfaces · Prof. R. Lipowsky	96
Wetting Transitions of Hydrocarbons on Water · Dr. W. Fenzl	98
Mesosopic Simulations of Biomimetic Membranes · Dr. J. Shillcock	100
Giant Vesicles – Helping us to Understand Biological Membranes · Dr. R. Dimova	102
New Membrane Physics with Polymersomes · Dr. H.-G. Döbereiner	104
Emmy Noether Junior Research Group · Dr. U. Schwarz	106
Adhesion Behaviour of Vesicles at Finite Temperature · Dr. T. Gruhn	108
Membrane Adhesion · Dr. T. Weikl	110
Protein Folding Kinetics · Dr. T. Weikl	111

Polyelectrolytes · Dr. C. Seidel	112
Semiflexible Polymers and Filaments · Dr. J. Kierfeld	114
Molecular Motors and Active Systems · Prof. R. Lipowsky	116
Theoretical Evolutionary Ecology · Dr. A. Valleriani	118
<b>BIOMATERIALS</b>	
Research in the Department of Biomaterials · Prof. P. Fratzl	122
<b>APPENDIX</b>	
<b>Organigramm</b> <b>Organization Chart</b>	128
<b>Fachbeirat</b> <b>Scientific Advisory Board</b>	130
<b>Drittmittelprojekte</b> <b>Third Party Funds</b>	131
<b>Wissenschaftliche Veranstaltungen</b> <b>Scientific Events</b>	138
<b>Wissenschaftliche Abschlüsse und Preise</b> <b>Degrees and Awards</b>	140
<b>Wissenschaftliche Veröffentlichungen und Patente</b> <b>Publications and Patents</b>	142

## Vorwort



Wolfgang Ostwald, einer der Begründer der Kolloidchemie, bezeichnete die Kolloid- und Grenzflächenforschung 1914 noch als „eine Welt der vernachlässigten Dimensionen“, und bis vor wenigen Jahren hatte diese Aussage tatsächlich noch ihre Berechtigung. Doch was verstehen wir eigentlich unter Kolloiden?

Kolloide sind Einheiten fein verteilter Materie mit Dimensionen vom Nanometer bis in den Mikrometerbereich und besitzen ein hohes Oberflächen/Volumen Verhältnis. Sie sind allgegenwärtig in der belebten Natur (Blut, Milch, Zellen) und auch überall in der technischen Welt (Farben, Tinten, Medikamente), in der Mikroelektronik oder in Baustoffen. Viele Aspekte der Kolloidforschung sind daher schon untersucht worden. Warum gründete man also vor 11 Jahren ein Institut, welches sich mit den Grundlagen in diesem Forschungsbereich befasst?

Chemie und Physik beschäftigten sich bis vor wenigen Jahren mit der Herstellung und dem Verständnis von Strukturen auf der molekularen Ebene („molekulare Wissenschaften“) sowie der makroskopischen Ebene (Festkörperforschung). Sowohl die Längenskalen dazwischen als auch ihre Hierarchien blieben dabei im Wesentlichen unberücksichtigt.

Heute dagegen finden wir in der Chemie eine starke Tendenz, immer größere Strukturen zu präparieren und deren Anlagerung zu kontrollieren. Zudem lernt die Physik, makroskopische Strukturen zu miniaturisieren und mit Vakuumtechniken Übergitter in allen Dimensionen zu konstruieren. 1997 wurde dieser „Wettlauf um die Mesoskala“ dann zu einem öffentlichen, politisch-gesellschaftlichen Phänomen und wurde mit dem Schlagwort „Nanowissenschaften“ belegt. Die Durchdringung ist mittlerweile so hoch, dass die Gesellschaft dieses spezielle Wissenschaftsfeld als eines ihrer wichtigsten Hoffnungsträger versteht. Dies ist eine Entwicklung, die 1992 noch nicht vorherzusehen war, aber das Institut mit seinen so zentral nanowissenschaftlichen Aktivitäten, vergleichsweise früh bestätigt hat.

Kann sich das Institut nun deutschland- und weltweit mit anderen Aktivitäten des Feldes messen? Dieses Urteil steht uns nicht zu, aber wir wollen die Öffentlichkeit neben unseren speziell wissenschaftlichen Publikationen mit dieser Broschüre über die Forschungsaktivitäten der letzten zwei Jahre informieren.

Das Feld der Kolloide und Grenzflächen ist hochgradig multidisziplinär und berührt viele Fachdisziplinen mit ihren speziellen Sprachen und intellektuellen Kulturen, die nicht immer verständlich sind. Daher haben wir für alle Abteilungen eine generelle Einführung vorangestellt, in der die Arbeitsweise und Motivation der Arbeit, gefolgt von kurzen Fortschrittsberichten, vorgestellt werden. Lernen Sie eine Welt voll mit verschiedenen Eindrücken kennen: biomimetische Prozesse, Selbst-Organisation, neue Messtechniken mit vorher nicht gekannter Auflösung, die Konstruktion künstlicher Zellen, neue theoretische Ansätze, Skalenkopplung und neue Algorithmen für numerische Modelle.

Damit verzahnt ist die Welt der Anwendungen: Pharmazie, Medizin, Informationstechnologie, Katalyse, Kosmetik, neue Baustoffe sowie umweltfreundliche Prozesse. Aber auch „Klassiker“ wie Farben oder Lacke gehören zu den Feldern, die direkt oder indirekt von den Arbeiten des Institutes profitieren. Obwohl die Max Planck Forschung sich streng mit den Grundlagenaspekten der Wissenschaft befasst, ist es die Alltagsbedeutung unseres Forschungszweiges, der eben auch akademisches Lernen direkt anwendbar macht. Lesen Sie die Broschüre und fragen sie einfach den zuständigen Wissenschaftler nach weiteren Details. Zusätzliche Informationen erhalten sie auch auf den Webseiten des Institutes: ([www.mpikg-golm.mpg.de](http://www.mpikg-golm.mpg.de))

Zahllose Kooperationen mit den vier lokalen Universitäten, nationale und internationale Kooperationen und Gäste sowie Dutzende von Industrieprojekten (in der Mehrzahl ohne öffentliche Gelder) zeigen, dass der Dialog zwischen Wissenschaft und Öffentlichkeit gefördert und sich für die daraus resultierenden Bedürfnisse und Sorgen eingesetzt wird. Überprüfen sie auch dies und suchen sie nach Antworten für ihre Fragen oder gar Partner für ihre Projekte!

Besonders die letzten zwei Jahre brachten enorme Änderungen. Besonders hervorzuheben sind die Gründung der Internationalen Max Planck Forschungsschule für Biomimetische Systeme und die Realisierung der vierten Abteilung des Institutes unter Leitung von Peter Fratzl, die uns in Richtung Materialien, Analytik und Ingenieurwissenschaft ergänzen wird.

Das Institut feiert am 26. November 2003 seinen elften Geburtstag, und drei Direktoren sind seit nun zehn Jahren im Amt. Die Nachwehen des Umzugs und die Integration der beiden Standorte 1999 fielen noch in den Berichtszeitraum, und der vorliegende Bericht ist eines der ersten wirklich gemeinsam erarbeiteten Dokumente. Wohl ein Zeichen einer Transformation, die nach langer Zeit ihren Abschluss fand, aber sicher auch ein guter Ausgangspunkt, um auf das Bisherige zurückzublicken und sich auf den kommenden Weg zu freuen.

Prof. Dr. Dr. h. c. Markus Antonietti  
Geschäftsführender Direktor 2001-2002

# Preface

Wolfgang Ostwald, often regarded as the founder of colloid chemistry, described the subject of interface and colloid science already in 1914 as that of a “world of neglected dimensions”, and this was true still some few years back. But what exactly are colloids?

Colloids are entities with dimensions in the nanometer to micrometer range and possess a high surface-to-volume ratio. They are ubiquitous in life, e.g. in cells, blood or milk, but also in the technical world such as paints, inks, displays, drugs, cement, etc.. Many aspects of colloid science are obviously already well examined, so why was it timely 11 years ago to found an institute focussing on basic science in this field?

Up to some years ago, chemistry and physics had developed very strongly to prepare and understand structures on the molecular level (“molecular sciences”) and on the macroscopic level (“solid state sciences”), but all length scales and the hierarchies in between were essentially neglected.

Nowadays, there is on the one hand a strong tendency in chemistry to prepare larger tectonic units and to design well defined molecular assemblies; on the other hand physics miniaturizes macroscopic structures and builds-up superlattices in all dimensions by vacuum techniques. In 1997 this run on the mesoscale became a public phenomenon and was rephrased as “nanosciences”. Meanwhile society regards this special research area as one of the scientific and technological “hopes” for a better future. This wave could not have been predicted in 1992, and it is still an open question how to handle it to keep the science. At least it is a rather early justification for the existence our institute being in the very middle of a number of those activities.

How is the institute positioned amongst all other activities in this area in Germany and worldwide? Well, this is not ours to decide, but we can inform the public along our special scientific papers, for instance with this booklet, which summarizes the scientific activities of the MPI of Colloids and Interfaces of the years 2001 and 2002.

The field of colloids and interfaces is highly multidisciplinary and involves a number of disciplines with all their specific languages and modes of information, not necessarily persuasible by the public. This is why you will find for each of the departments a more general header on “working philosophy” and motivation, followed by short progress reports where the scientists give specific information about their own projects. You will learn about a world full of different flavours: biomimetic processes, self-organization of matter, new instrumental techniques with unparalleled information and resolution, the integration of components towards artificial cellular objects, new theoretical models, the coupling of scales, and numerical modelling with new algorithms.

Interlocked is the world of applications: fields such as pharmacology, medicine, information technology, catalysis, cosmetics, new construction materials, non polluting processes, but also very traditional applications as paints, coatings, or detergents are directly or indirectly touched by projects of the institute. Although the Max Planck research is strictly related to fundamental aspects of science, it is the relevance of the field which makes even academic observations sometimes directly applicable. Learn about it by reading this brochure and contact the responsible scientists for further details! Additional information is available under the web pages of the institute: [www.mpikg-golm.mpg.de](http://www.mpikg-golm.mpg.de) and the pages of individual researchers.

The institute as a whole is very open to the public, as illustrated by numerous collaborations with the four universities in the area, national and international collaborations and visitors, and dozens of co-operations with industry (in a larger number without public payment). It is the institute’s policy to be open towards outer need and concern, so find out if there is potential for your co-operations or some answers to your questions.

The last two years brought enormous changes, among others the constitution of the International Max Planck Research School on Biomimetic Systems and the establishment of the fourth department, headed by Peter Fratzl, who will expand the institute’s profile towards materials, analysis and engineering.

I would also like to announce that the institute celebrates its 11th year of existence on November 26, 2003 and three directors got over ten years of service. It is that the integration of the two former sites (up to 1999) into one institute still fell into the years of report, and the present document is one of the first we ever jointly produced. This is an outer sign for a transformation which took a long time to perform, but also a viewing point to review our previous activities and to look out to the way in the next forthcoming years.

Prof. Markus Antonietti  
Managing Director 2001-2002

## Rückschau – Die ersten elf Jahre



Nach der deutschen Vereinigung evaluierte der Wissenschaftsrat die Institute der ehemaligen Akademie der Wissenschaften der DDR. Er kam u.a. zu dem Ergebnis, dass in den Instituten für Physikalische Chemie und für Organische Chemie in Berlin-Adlershof und für Polymerchemie in Teltow viel versprechende Aktivitäten existierten, die in ein neu zu gründendes Max-Planck-Institut für Kolloid- und Grenzflächenforschung integriert werden könnten.

Diesen Vorschlag griff eine Kommission der Max-Planck-Gesellschaft auf, die großes Potential und Nachholbedarf für die Grundlagenforschung in diesem Gebiet zwischen den Disziplinen Chemie, Physik und Biologie sah, und so wurde das Max-Planck-Institut für Kolloid- und Grenzflächenforschung am 01.01.1992 gegründet.

Bei der Gründung des Institutes wurde ein Neubau vorgesehen, in den die vorübergehend in Berlin-Adlershof und Teltow untergebrachten Gruppen schließlich im April 1999 einzogen. Eine zunächst eingerichtete Außenstelle in Freiberg wurde in die dortige TU eingegliedert. Die drei Max-Planck-Direktoren Prof. Kahlweit, Prof. Kampa und Prof. Spieß übernahmen die kommissarische Leitung. Dies beinhaltete vor allem den Aufbau von Verwaltung, Infrastruktur und Personalentscheidungen, da ein Großteil der vorgesehenen 100 Planstellen unmittelbar zu besetzen waren. Die kommissarische Leitung wurde beratend unterstützt von Prof. Kretzschmar und Prof. Philipp, die an den beiden Standorten früher leitend tätig waren.

Am 01.10.1993 bzw. 01.11.1993 übernahmen die Gründungsdirektoren Prof. Antonietti, Prof. Lipowsky und Prof. Möhwald die kollegiale Leitung des Instituts und gaben ihm seine wissenschaftliche Ausrichtung und die jetzige Struktur mit den Abteilungen „Grenzflächen“ (H. Möhwald), „Kolloidchemie“ (M. Antonietti) und „Theorie“ (R. Lipowsky). Auf die Gründung der vorgesehenen vierten Abteilung „Biomaterialien“ wurde zunächst aus Mangel an freien Stellen und Raum verzichtet. Stattdessen wurde eine Nachwuchsgruppe zu „Benetzung“ im Institut angesiedelt. Nach Wegberufung des Stelleninhabers (Prof. Herminghaus) wurde diese Gruppe aufgelöst, und am 01.02.03 hat die vierte Abteilung unter Prof. P. Fratzl ihre Arbeit aufgenommen.

Die Gründungsdirektoren transferierten einen Teil ihrer bisherigen Gruppen in Jülich, Mainz und Marburg nach Berlin bzw. Teltow und stellten mehrere Habilitanden ein, mit denen sie neue Gebiete angingen. Damit ergaben sich erhebliche Integrationsaufgaben West/Ost, Jung/Alt neben der Vielfalt von Disziplinen und Denkansätzen. Das Institut war zu internationalisieren in Richtung West-Europa und Übersee, und mittlerweile sind ein Drittel der Mitarbeiter Ausländer. Es wuchs auf 240 Mitarbeiter innerhalb der ersten sechs Jahre an, und diese Mitarbeiterzahl kann aus Raumgründen nicht mehr nennenswert gesteigert werden

(Die Ressourcen für die vierte Abteilung wurden frei durch Pensionierungen und Schrumpfen der bestehenden Abteilungen).

Nach dem Einzug in Golm bei Potsdam konnten die Abteilungen besser verknüpft werden und die Infrastruktur im Institut weiter ausgebaut werden, wobei vor allem die Verwaltungsleiterin Frau R. Schlender sich viele Verdienste erwarb. Enttäuschend langsam schreitet die Entwicklung des Wissenschaftsparks Golm voran mit den zentralen Problemen Verkehrsanbindung, soziale und Einkaufsmöglichkeiten, Innovations- und Gründerzentrum.

Begründung für die Wahl des Standorts Golm war, dass auch die naturwissenschaftliche Fakultät der Universität Potsdam dort angesiedelt wird. Deren Ausbau ist in vollem Gange, und die Direktoren und mehrere Mitarbeiter sind an der Lehre in den Fachbereichen Physik und Chemie beteiligt. Mittlerweile steigen in diesen Fächern auch die Studentenzahlen und wir hoffen, bald auch die ersten Potsdamer Diplomanden auszubilden. Die in Deutschland sinkenden Doktorandenzahlen konnten durch verstärkte Anwerbung im Ausland kompensiert werden, so dass diese Zahl im Institut nie unter sechzig fiel.

Das Institut ist im Großraum Berlin vernetzt, insbesondere durch einen Sonderforschungsbereich mit Beteiligung aller Universitäten („Mesoskopische Verbundsysteme“) und über gemeinsame Projekte an den Berliner Neutronen- und Synchrotronstrahlungsquellen (Hahn-Meitner-Institut, BESSY), im nationalen Bereich existieren viele Verbundprojekte mit Hochschulen, Instituten und Industrie. Da die eigene Stärke die Grundlagenforschung ist und bleibt, werden neue Wege erprobt, diese außerhalb des Instituts zur Anwendung zu bringen. Dazu gehören neben den traditionellen Verbundprojekten mit Firmen auch die Hilfe bei Ausgründungen (bisher sechs) und eine gemeinsame Forschergruppe mit dem benachbarten Fraunhofer-Institut für Angewandte Polymerforschung. Neben der Beteiligung an EU-Programmen dienen der internationalen Vernetzung auch das gemeinsame Deutsch-Chinesische Labor in Peking, eine Deutsch-Französische Forschergruppe und vor allem die „International Max Planck Research School on Biomimetic Systems“, in der wir eine Doktorandenausbildung an der Universität Potsdam in englischer Sprache anbieten.

Aufgrund der hervorragenden Qualifikationen unserer Mitarbeiter und der ausgezeichneten Ausstattung konnten wir die nachlassende Förderung durch die Max-Planck-Gesellschaft ausgleichen, so dass mittlerweile etwa 30% des Etats von 12 Millionen Euro durch Drittmittel finanziert ist.

Die wissenschaftlichen Erfolge, die später beschrieben werden, schlugen sich bisher in ca. 3000 Publikationen nieder. Viel wichtiger aber ist der Wissenstransfer über Köpfe, d.h. die ca. 150 Doktoranden und ein Dutzend Professoren, die im Institut ausgebildet wurden. Wir vergessen aber auch nicht die Beiträge von Mitarbeitern, die nicht zu Karriere sprüngen führten, da sie entweder gleichwertige Positionen erreichten oder in Rente gingen. Ihnen war das Institut (hoffentlich) eine interessante Arbeitsstelle.

Prof. Dr. Helmuth Möhwald



## Looking Back – The First Eleven Years

After the German unification the Science Council evaluated the institutes of the former GDR Academy of Sciences. They concluded that there were most promising activities in the institutes of Physical Chemistry and Organic Chemistry in Berlin-Adlershof and of former Polymer Chemistry in Teltow that could be integrated into a prospective Max Planck Institute of Colloids and Interfaces. This proposal was taken up by a committee of the Max Planck Society that realized a large potential and need for basic science in this area between physics, chemistry and biology. Hence the Max Planck Institute of Colloids and Interfaces was founded on 01.01.1992.

After founding the institute new buildings were anticipated, and into these the groups with preliminary housing in Berlin-Adlershof and Teltow could move in April 1999. An outstation in Freiberg, initially also set up was meanwhile moved to the TU there. The preliminary leadership was taken over by the Max Planck directors Prof. Kahlweit, Prof. Kampa and Prof. Spieß. Their main task was to build up the administration and the infrastructure and to decide on personnel because most of the 100 positions foreseen for the institute had to be filled as soon as possible. The preliminary leadership was supported by advice from Prof. Kretzschmar and Prof. Philipp who have been previously in leading positions at the two locations.

On 01.10.93 and 01.11.1993 the founding directors Prof. Antonietti, Prof. Lipowsky and Prof. Möhwald took over the joint leadership of the institute and gave it its scientific directions and present structure with the departments "Interfaces" (H. Möhwald), "Colloid Chemistry" (M. Antonietti) and "Theory" (R. Lipowsky). The planned forth department "Biomaterials" was not yet set up because of a lack of free positions and space. Instead a junior group on "wetting" was installed. After the group leader (Prof. S. Herminghaus) had accepted a call on a chair the group ceased to exist, and on 01.02.03 the forth department under Prof. P. Fratzl has been started.

The founding directors transferred part of their previous groups in Jülich, Mainz and Marburg to Berlin and Teltow and hired young scientists seeking an academic career to enter into new research areas. This resulted in enormous tasks to integrate east/west, old/young together with a multiplicity of disciplines and ways of thinking. The institute had to be internationalized towards Western Europe and overseas, and meanwhile one third of the co-workers are foreigners. It grew towards 240 employees within the first six years and this number cannot be increased considerably because of a lack of space (The resources for the forth department result from retirement and shrinking of existing departments).

After rooming-in in Golm/Potsdam links between the departments could be improved and the infrastructure could be extended considerably. The latter task merits much to our administrative head Mrs. R. Schlender. Disappointingly slow has been the development of the "Science Park Golm" with main problems being commuting, social and shopping centres and an innovation and founder's centre.

The reason for choosing Golm as institute's location was that the science faculty of the University Potsdam was decided to move there. This move is well under way, and the directors and many co-workers are involved in teaching in physics and chemistry there. Meanwhile also the numbers of students in these subjects increase and we hope to train soon also the first diploma students from Potsdam. The in Germany decreasing number of PhD students could be compensated by hiring more students from foreign countries, so that the number never decreased below 60.

Integration in the greater Berlin area occurs predominantly via a „Sonderforschungsbereich" with participation of all universities (mesoscopic composites) and via joint projects using Berlin Neutron and Synchrotron radiation sources (Hahn Meitner Institute, BESSY), nationwide there are many joint projects with universities, institutes and industry. Since the own strength and mission is and remains basic science alternative ways are probed to link with applications outside the institute. Among them are besides traditional collaborative projects with companies, help with the foundation of start-ups (up to now six) and a joint research group together with the neighbouring Fraunhofer-Institute for Applied Polymer Research. Besides taking part in EU programmes international networking is also achieved via a joint German-Chinese International Laboratory in Beijing, a German-French Collaborative Research Group and, above all, via the "International Max Planck Research School on Biomimetic Systems". There we offer graduate education in English at the University Potsdam.

Since we have highly qualified co-workers and are well-equipped we have been able to compensate slightly decreasing funding by the Max Planck Society such that meanwhile 30% of our budget of 12 million EUR is financed from external sources.

The scientific success to be described below resulted in about 3000 publications, more importantly transfer of knowledge occurred via heads, i.e. about 150 PhD and a dozen professors have been trained in the institute. However, we also will not forget those contributions of co-workers which did not lead to career steps, because they received equivalent positions or retired. Hopefully for them the institute has been an exciting place to work at.

Prof. Helmuth Möhwald



# Das Forschungsprogramm des Max-Planck-Institutes für Kolloid- und Grenzflächenforschung

## Strukturelle Hierarchien in Bio-Systemen

Biologische Systeme sind überaus komplex und umfassen viele Stufen der Selbstorganisation. Die elementarsten dieser Stufen entsprechen den kolloidalen Domänen der Biomaterie, welche sich von den Molekülen bis hin zu den Zellen erstrecken (Abb.1) und den Übergangsbereich zwischen Materie und Leben darstellen.

Die erste Ebene in Abb.1 besteht aus relativ kleinen Molekülen, sogenannten Monomeren. Diese Monomere können nach ihrem chemischen Aufbau in verschiedene Gruppen eingeteilt werden. Beispiele sind die Gruppen, die aus 20 Aminosäuren bzw. aus vier Nukleotiden bestehen. Verschiedene Elemente jeweils einer Gruppe verbinden sich kovalent zu Polymeren wie Proteinen, Nucleinsäuren und Polysacchariden.

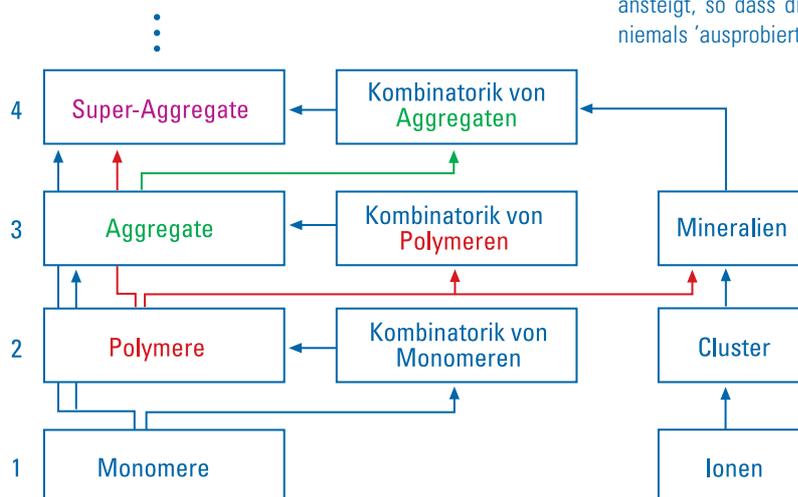


Abb. 1: Strukturelle Hierarchie von biologischen und biomimetischen Systemen im Bereich von Kolloiden und Grenzflächen. Der Hauptpfad auf der linken Seite führt von kleinen Molekülen oder Monomeren bis zu Super-Aggregaten, die verschiedene Molekülaggregate enthalten. Dagegen führt der Pfad auf der rechten Seite zu kleinen Mineralpartikeln, die durch adsorbierende Polymere stabilisiert werden.

Die Polymere bilden supramolekulare Aggregate wie z.B. Filamente, Membranen und Ribosomen. Filamente sind aus einer einzelnen Protein-Komponente aufgebaut, während Membranen neben Lipid- auch verschiedene Protein- und Polysaccharid-Komponenten enthalten. Ribosomen bestehen aus ca. 50 Proteinen und RNA. Zusätzlich zu diesen Polymeraggregaten können biologische Systeme auch kleine Kristalle und Minerale enthalten.

Schließlich lagern sich verschiedene Aggregate aneinander und bilden Super-Aggregate. Ein einfaches Beispiel dafür ist eine Lipidvesikel, die an ein Filament mittels eines Proteinmotors gebunden ist.

## Kolloide, Grenzflächen, Biomimetische Systeme

Sämtliche biologische Strukturen, die in Abb. 1 dargestellt sind, stellen kolloidale Strukturen dar, die von Grenzflächen umrandet werden. Entsprechend kann man Kolloide und Grenzflächen, die in ein flüssiges Medium eingebettet sind, als biomimetische Systeme bezeichnen. Ganz besonders trifft dies zu, wenn es sich bei der Flüssigkeit um Wasser handelt.

Die Strukturen, aus denen biologische Systeme aufgebaut sind, haben sich über eine sehr lange Zeit entwickelt. Während dieser Evolution haben nur wenige Typen von Monomeren, Polymeren und Aggregaten 'überlebt' und stellen heute die Bausteine für die biologischen Zellen dar. Eine solche Selektion fand bereits auf der niedrigsten Ebene der Monomere statt: Während die Biologie nur 20 Aminosäuren nutzt, ist die Chemie in der Lage, über 70 solcher Moleküle zu synthetisieren. Hinzu kommt noch, dass die Anzahl der möglichen Strukturen mit der Anzahl der Bausteine exponentiell ansteigt, so dass die überwiegende Zahl dieser Strukturen niemals 'ausprobiert' wurde.

Es gibt mehrere Strategien, mit denen man biomimetische Systeme aufbauen kann. Erstens kann man sich darauf beschränken, die grundlegenden Konstruktionsprinzipien biologischer Systeme möglichst einfach nachzuahmen. Diese Strategie führt z.B. zur Bildung von Homo-Polymeren, die nur aus einem Monomer bestehen, oder zu Lipid-Doppelschichten, die nur eine Lipidkomponente enthalten. Zweitens kann man biologische Teilsysteme nachbauen, die eine relativ kleine Anzahl von Komponenten umfassen, und drittens gibt es die Möglichkeit hybride Systeme zu bilden, die Kombinationen von natürlichen und synthetischen Komponenten enthalten.

## Aktuelle Forschung

Die gegenwärtige Forschung am Max-Planck-Institut für Kolloid- und Grenzflächenforschung konzentriert sich auf die Synthese und den Aufbau von komplexeren Systemen, welche multifunktional sind und mehrere Aspekte biologischer Systeme gleichzeitig imitieren.

Diese Forschung, die sich an den Grenzen von Physik, Chemie, Material- und Biowissenschaften bewegt, beinhaltet folgende Aktivitäten: Synthese und Aufbau von experimentellen Modellsystemen; experimentelle Charakterisierung dieser Systeme; äußere Felder und strukturelle Stabilität; Kontrollparameter und strukturelle Transformationen; Formulierung und Analyse von theoretischen Modellen; Identifikation grundlegender Mechanismen sowie allgemeiner Prinzipien, die das kooperative Verhalten dieser Systeme bestimmen.

Das Wechselspiel von experimenteller und theoretischer Forschung ist für ein grundlegendes Verständnis dieser Systeme notwendig. Erst dieses Verständnis versetzt uns in die Lage, den Aufbau dieser Systeme systematisch zu verbessern, ihre Leistung zu optimieren und ihre Zuverlässigkeit zu erhöhen. Auf diese Weise liefert die Kolloid- und Grenzflächenforschung von heute die Grundlagen für die technischen Anwendungen von morgen.

## Die Bildung von Kolloiden und Grenzflächen

Im Allgemeinen gibt es zwei verschiedene Wege um kolloidale Strukturen zu erhalten: Bottom-up und Top-down Methoden. Zu den Bottom-up Methoden zählen Polymerisation, Selbstaggregation sowie Partikelnukleation und -wachstum, zu den Top-down Ansätze dagegen Zerkleinern, Bedrucken, Lithographie und ‚Prototyping‘.

Die Chemie bietet viele Ansätze zur Synthese von Polymeren. Ein aktuelles Thema sind Diblockkopolymere, die zwei unterschiedliche Monomerblöcke besitzen. Ist der eine Block hydrophob und der andere hydrophil, können sich diese amphiphilen Polymere zu Doppelschichten und Vesikel zusammenlagern. Wenn dagegen ein Block schwach und der andere stark hydrophil ist, adsorbieren die Kopolymere an den Oberflächen von Partikeln und Mineralien und verändern deren Wachstums-Morphologien. Die Größe und Gestalt derartiger Partikel kann dadurch kontrolliert werden, dass man die Wachstumsprozesse in entsprechenden Kompartimenten ablaufen lässt.

Amphiphile Moleküle und Polymere, die in einem flüssigen Medium verteilt sind, lagern sich spontan zu verschiedenen Aggregaten zusammen, so z.B. zu Mizellen und Doppelschichten. Zusätzlich sind diese Moleküle oberflächenaktiv und besitzen eine starke Tendenz an flüssigen Grenzflächen zu adsorbieren. Lipid-Doppelschichten werden in der Abteilung Theorie, Lipid-Monoschichten in der Abteilung Grenzflächen untersucht.

Kolloidale Strukturen sind durch relativ große Grenzflächenanteile charakterisiert. Daher führt die Bildung von Kolloiden gleichzeitig zur Bildung von Grenzflächen. Zusätzlich können ausgedehnte und strukturierte Grenzflächen mit verschiedenen Top-down Methoden erzeugt werden.

Grenzflächen lassen sich funktionalisieren, indem man zusätzliche Moleküle und Partikel anheftet oder einlagert. Eine sehr leistungsfähige Methode, mit der man vielschichtige Grenzflächenstrukturen aufbauen und funktionalisieren kann, basiert auf der alternierenden Beschichtung mit negativ und positiv geladenen Polyelektrolyten.

## Biomimetische Kompartimente und Gerüste

Biologische Systeme besitzen Hierarchien von Kompartimenten und Gerüsten. Auf der kolloidalen Ebene handelt es sich um Membran-Kompartimente und Filament-Gerüste. Die Hauptfunktion der Membran-Kompartimente besteht darin, verschiedene, voneinander getrennte Raum-Bereiche zu schaffen. Die räumliche Anordnung dieser verschiedenen Kompartimente wird von den Filament-Gerüsten bestimmt.

Die Forschung am MPI für Kolloid- und Grenzflächenforschung beschäftigt sich mit der Bildung und dem Studium verschiedener Arten von Kompartimenten: Tröpfchen in Mikro- und Miniemulsionen, Vesikel aus Lipiden oder Block-Kopolymeren sowie Kapseln aus Polyelektrolyt-Schichten. In jedem dieser Kompartimente werden physikalische und chemische Strukturbildungs-Prozesse durchgeführt und analysiert.

Darüber hinaus werden zwei Arten von relativ steifen Gerüsten benutzt: die Abteilung Kolloidchemie bedient sich mesoporöser Materialien, die Poren im Nanobereich aufweisen, die neue Abteilung Biomaterialien wird Gerüste im Mikrometerbereich nutzen, die durch schnelles Prototyping erzeugt werden.

Am MPI wird auch ein großes Spektrum an experimentellen Methoden eingesetzt, um die Struktur und Dynamik von Kolloiden und Grenzflächen zu charakterisieren. Zusätzlich werden verschiedene Methoden der chemischen Analyse angewandt. Weiterführende Informationen finden sich in den einzelnen Abteilungsberichten.

## Strukturelle Transformation von Kolloiden und Grenzflächen

Auf jeder Hierarchieebene der **Abb. 1** begegnet man strukturellen Transformationen: Polymere verändern ihre Konformation, Membranen ihre Morphologie oder Topologie und Multischichten aus Polyelektrolyten ihre Maschengröße und Permeabilität; mehrkomponentige Systeme durchlaufen Entmischungsprozesse, was zur Bildung interner Domänen führt; Super-Aggregate wie Filamentbündel durchlaufen entropisch getriebene Entbindungsvorgänge.

Diese strukturellen Transformationen lassen sich einerseits global durch Änderung von Temperatur, pH und osmotischen Bedingungen induzieren, andererseits lokal durch Manipulation einzelner Kolloide mit entsprechenden Sonden.

Ein langfristiges Ziel besteht in der verbesserten Kontrolle dieser strukturellen Transformationen. Insbesondere möchte man die Strukturen zwischen den verschiedenen (meta)stabilen Zuständen hin und her schalten. Ein Beispiel dafür ist die Nutzung aktiver Prozesse, die von exergonen chemischen Reaktionen angetrieben werden.

### Theorie der Kolloide und Grenzflächen

Die Thermodynamik der Kolloide und Grenzflächen liefert einen allgemeinen und leistungsfähigen Top-down Zugang, der nur von einer relativ kleinen Anzahl von Parametern abhängt. Eine Grenzfläche beispielsweise kann durch ihren Laplacedruck, ihre Grenzflächenspannung sowie ihre Kontaktwinkel charakterisiert werden. Ebenso kann die großskalige Morphologie von Membranen innerhalb des gleichen theoretischen Grundgerüsts verstanden werden, wenn man Krümmungsterme mitberücksichtigt. Im einfachsten Fall umfasst diese Erweiterung nur einen zusätzlichen Parameter, und zwar die Biegesteifigkeit der Membran.

Der Bottom-up Zugang benutzt Modelle für Monomere und ihre Wechselwirkungen, die mit den theoretischen Methoden der statistischen Mechanik untersucht werden. Auf diese Weise lassen sich statische und dynamische Eigenschaften von Polymeren, Aggregaten und Super-Aggregaten berechnen. Ein wichtiges Werkzeug sind dabei auch Computeralgorithmen, mit denen man die entsprechenden Strukturbildungsprozesse simulieren kann.

Das langfristige Ziel dieser Theorien besteht darin, die grundlegenden Mechanismen und allgemeinen Prinzipien zu identifizieren, die das Verhalten von Kolloiden und Grenzflächen bestimmen. Dabei geht es insbesondere um ein tieferes Verständnis von strukturellen Transformationen, entropischen Kräften sowie aktiver Prozesse, die durch chemische Reaktionen angetrieben werden.

### Neue Forschungsthemen

Schließlich möchte ich noch auf einige neue, sehr attraktive Forschungsthemen des MPI für Kolloid- und Grenzflächenforschung verweisen.

- Physik und Chemie in Nanokompartimenten: Diese Aktivität ist auf die Konstruktion von "Nanolabs" ausgerichtet, die in intelligente Grenzflächen eingebettet sind. Dabei geht es unter anderem um kontrollierte Strukturbildungsprozesse sowie um die kombinatorische und evolutionäre Chemie in derartigen Kompartimenten.
- Multifunktionale Biomaterialien: Im Allgemeinen können biomimetische Systeme auf allen Strukturebenen mit biologischen Systemen in Wechselwirkung treten. **(Abb.2):** Synthetische Polymere können sich an Zellrezeptoren und andere Biopolymere binden; Aggregate können über Membranprozesse in die Zellen importiert und an bestimmte Organellen transportiert werden; synthetische Gerüste können für die räumliche Anordnung von Zellen in künstlichem Gewebe genutzt werden. Es wäre sehr sinnvoll, diese verschiedenen Ebenen in neue multifunktionale Biomaterialien zu integrieren, die hierarchisch organisiert sind und bei denen man die Wechselwirkungen auf den verschiedenen Strukturebenen unabhängig schalten kann.

### Wechselwirkungen

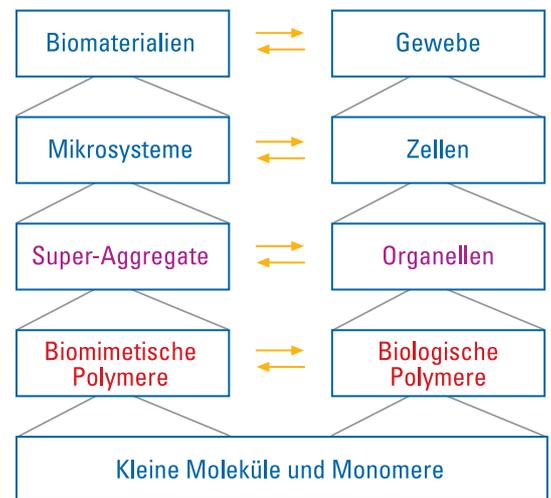


Abb.2: Strukturelle Hierarchie biomimetischer und biologischer Systeme, die der linken und rechten Säule entsprechen. Die beiden Systemarten können auf allen Ebenen zueinander in Wechselwirkung treten.

- Aktive Biomimetische Systeme: Die Vielseitigkeit biologischer Systeme ist sehr eng mit der Tatsache verknüpft, dass diese Systeme aktiv sind und ihre räumliche Struktur auf der Nano- und Mikroskala umbauen können. Diese Fähigkeit gründet sich auf aktive Nanostrukturen wie Filamentmonomere und molekulare Motoren, die exergone chemische Reaktionen katalysieren. Diese aktiven Prozesse können seit kurzem in biomimetischen Modellsystemen nachgeahmt und systematisch untersucht werden.

Prof. Dr. Reinhard Lipowsky

# The Research Program of the Max Planck Institute of Colloids and Interfaces

## Structural Hierarchy in Biological Systems

Biological systems are complex and contain many levels of self-organization. The lower levels correspond to the colloidal domain of biomatter which extends from molecules to cells, see Fig. 1, and which may be regarded as the twilight zone between matter and life.

The lowest level in Fig. 1 consists of relatively small molecules or monomers. These monomers can be divided into several subsets which contain chemically similar but distinct components. Examples are the subsets of 20 amino acids and of 4 nucleotides. Different elements of one subset can be connected by covalent bonds which leads to the formation of polymers such as proteins and nucleic acids.

## Colloids & Interfaces and Biomimetic Systems

All biological structures displayed in Fig. 1 represent colloids and interfaces. Vice versa, colloids and interfaces, which are embedded in a liquid medium, can be regarded as biomimetic systems. This applies in particular if the liquid is water.

The combinatorics indicated in Fig. 1 leads to extremely large numbers of possible colloidal structures. Indeed, if such a structure is build up from several components and contains  $N$  elements, the number of possible structures grows exponentially with  $N$ . This implies that the vast majority of possible colloidal structures have never been created in spite of the rather long time for biological evolution. Thus, there is plenty of room in the colloidal domain!

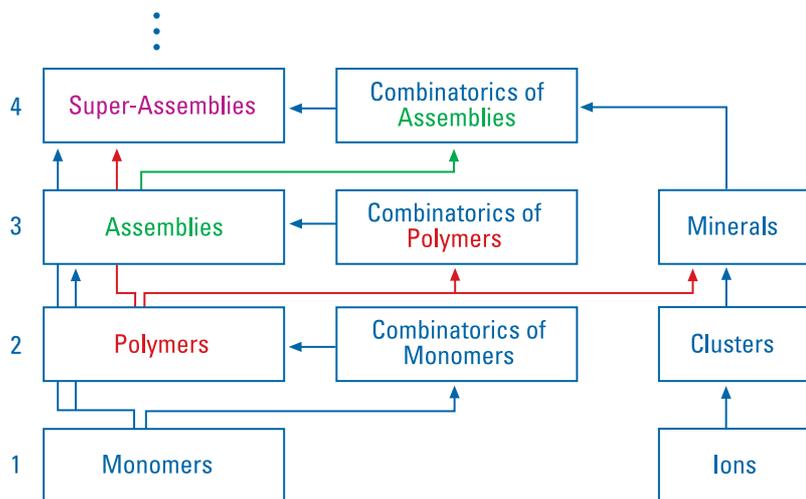


Fig. 1: Structural hierarchy of biological and biomimetic systems in the colloidal domain. The main pathway on the left proceeds from small molecules or monomers to super-assemblies, i.e., groups of interacting assemblies. The pathway on the right leads to small mineral particles which are stabilized by adsorbed polymers.

These polymers form supramolecular assemblies such as filaments, membranes, and ribosomes. Filaments are usually built up from a single protein component whereas membranes typically contain a large number of lipid components as well as proteins and polysaccharides. Ribosomes consist of about 50 proteins and RNA. In addition to these polymer assemblies, biological systems can also contain small crystallites and minerals. Finally, different types of assemblies may associate to form super-assemblies. A simple example is provided by a lipid vesicle which is bound to a filament via a motor protein.

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 homopolymers, 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.

### **Current Research on Colloids and Interfaces**

Current research at the MPI focuses on the synthesis and construction of multicomponent systems which are multifunctional and, thus, mimic several aspects of the biological systems at the same time.

This research, which lies at the borderline of physics, chemistry, materials science and bioscience, includes the following activities: Synthesis and construction of experimental model systems; Experimental characterization of these systems; External perturbations and structural stability; Control parameters and structural transformations; Construction and analysis of theoretical models; Identification of basic mechanisms and general principles which determine the cooperative behavior of these systems.

This interplay between experiment and theory is necessary in order to gain a deeper understanding of colloidal systems. This understanding can then be used in order to improve the design of these systems, to optimize their performance, and to increase their reliability. In this way, the research on colloids and interfaces as performed today at the MPI provides the basis for the technology of tomorrow.

### **Construction of Colloids & Interfaces**

In general, there are two different routes by which one can construct colloidal structures: Bottom-up approaches, and top-down approaches. The bottom-up approaches include polymerization, self-assembly, and particle nucleation and growth. The top-down approaches include dispersing, printing, lithography, and prototyping.

There are many methods of polymer synthesis which are applied in the Colloid Chemistry Department. One particularly interesting class of polymers consists of diblock copolymers. If one block is hydrophobic and the other is hydrophilic, one obtains amphiphilic polymers which can form bilayers and vesicles. If one block is weakly hydrophilic and the other is strongly hydrophilic, the copolymers can be used to change the morphology of growing particles and minerals. The size and shape of such particles can be controlled by performing these processes in nanocompartments.

Amphiphilic molecules and polymers, which are dispersed in a liquid medium, spontaneously self-assemble into various aggregates. One such aggregate are bilayer membranes which are studied in the Theory Department. In addition, these molecules are surface-active and have a strong tendency to adsorb at fluid interfaces. These monolayers are studied in the Interface Department.

All colloidal structures are characterized by a relatively large interfacial area. Therefore, the construction of colloids implies the formation of interfaces. In addition, large well-defined interfacial areas can be created by several top-down approaches.

Interfaces can be functionalized by decorating them with additional molecules and particles. A rather powerful method to create such interfacial structures, which has been developed by the Interface Department, is via the subsequent deposition of negatively and positively charged polyelectrolytes.

### **Biomimetic Compartments and Scaffolds**

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. The main function of filament scaffolds is to reshuffle these compartments and to reorganize their spatial arrangement.

Research at the MPI involves the construction and study of different types of compartments: droplets in micro- and miniemulsions, vesicles bounded by lipid or polymeric bilayers, and capsules bounded by polyelectrolyte multilayers. In all of these compartments, one can perform physical and chemical processes of structure formation and self-organization.

In addition, two types of rigid scaffolds are currently used: the Colloid Chemistry Department uses mesoporous materials which provide pores in the nanoregime, and the new Biomaterials Department will use scaffolds in the micrometer regime constructed by rapid prototyping.

A large spectrum of experimental methods is used at the MPI in order to characterize the structure and dynamics of colloids and interfaces. In addition, various methods of chemical analysis are applied. More details about these methods are provided in the reports of the experimental groups.

### **Structural Transformations**

On all levels of the hierarchy shown in **Fig. 1**, one encounters structural transformations: polymers can undergo transitions between different conformational states; assemblies such as membranes can undergo transitions between different morphologies; polyelectrolyte multilayers can undergo changes in their mesh size which leads to changes in the multilayer permeability; multicomponent systems can undergo phase separation which leads to the formation of internal domains; super-assemblies such as filament bundles can undergo unbinding transitions etc.

On the one hand, these structural transformations can be induced globally by changing temperature, pH, or osmotic conditions. On the other hand, such transformations may also be induced locally by manipulating single colloidal structures using nanotips, micropipettes, or the particle force apparatus.

One long-term goal is to gain improved control over these structural transformations. In particular, one would like to switch the structures back and forth between their different (meta)stable states. One particularly intriguing approach is to use active processes which are driven by exergonic chemical reactions.

## Theory of Colloids and Interfaces

The thermodynamics of interfaces and membranes provides a general and powerful top-down approach into the colloidal domain since it depends only on a relatively small number of parameters. An interface, for example, can be characterized by its Laplace pressure, its interfacial tension, and its contact angles. Likewise, one may use the same theoretical framework in order to describe the large-scale morphology of membranes provided one includes curvature terms. In the simplest case, this involves only one additional parameter, the bending rigidity of the membranes.

The bottom-up approach into the colloidal domain starts from coarse-grained models for the monomers and their interactions, which are studied by a wide range of theoretical methods as provided by statistical physics. In this way, one may calculate the static and dynamic properties of polymers, assemblies, and super-assemblies. One important tool is provided by computer algorithms by which one can simulate the corresponding processes of structure formation.

The main goal of these theories is to identify the basic mechanisms and the general principles which govern the behavior of colloids and interfaces. These basic mechanisms include external perturbations and structural transformations, Brownian motion and entropic forces, and active processes which are driven by chemical reactions.

## New Topics

Finally, I want to mention some new and highly appealing research topics of the MPI:

- Physics and Chemistry in Nanocompartments: One goal of this activity is the construction of 'nanolabs' which might be embedded in smart interfaces. These 'nanolabs' represent nanocompartments in which different physical and chemical processes can be induced. Likewise, it would be rather interesting to perform combinatorial and evolutionary chemistry in such compartments.
- Multifunctional Biomaterials: In principle, biomimetic systems can 'crosstalk' to biological systems on all levels, see **Fig. 2**: synthetic polymers can bind to cell receptors and other biopolymers; biomimetic assemblies can interact with the membranes and filaments of biological cells; synthetic scaffolds can be used for the spatial arrangements of cells into tissues. It would be rather useful to integrate these different levels into new multifunctional biomaterials which are organized in a hierarchical way and by which one can address, separately or simultaneously, the different structural levels of the biological systems.

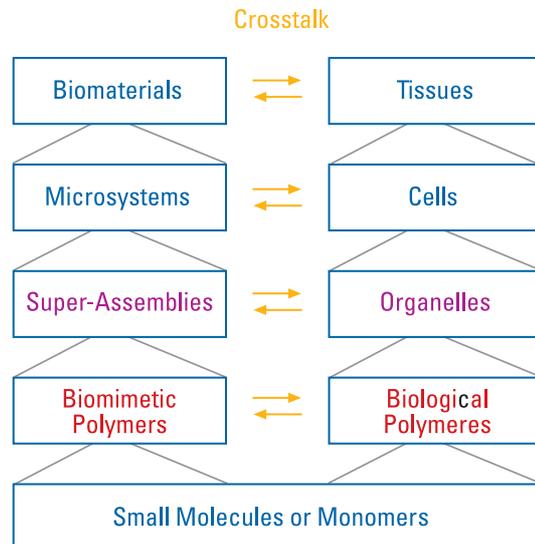


Fig. 2: Structural hierarchy of biomimetic and biological systems corresponding to the left and right column, respectively. Crosstalk between both types of systems can occur on all levels.

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

Prof. Reinhard Lipowsky

# Wissenschaftliche Beziehungen

## Nationale Kooperationen:

Das Max-Planck-Institut für Kolloid- und Grenzflächenforschung unterhält viele nationale Kooperationen mit Universitäten und wissenschaftlichen Instituten des Landes. Im Folgenden werden die bedeutendsten Zusammenarbeiten innerhalb der einzelnen Forschungsgebiete mit den dement-sprechenden Arbeitsgruppenleitern aufgelistet:

### • **Sonderforschungsbereich "Mesoskopische Verbundsysteme"**

eine Kooperation der Universität Potsdam und der drei Berliner Universitäten (M. Antonietti, H. Cölfen, D. G. Kurth, R. Lipowsky, H. Möhwald, H. Schlaad)

### • **DFG-Schwerpunkte (umfassen jeweils ca. 30 Gruppen)**

- Polyelektrolyte (G. Brezesinski, H. Dautzenberg, H. Möhwald, R. Netz, M. Schönhoff, C. Seidel)
- Benetzung und Strukturbildung (T. Fischer, R. Lipowsky, H. Riegler)
- Magnetische Flüssigkeiten (F. Caruso, K. Landfester)
- Photonische Kristalle (F. Caruso)
- Biominalisation (H. Cölfen)

### • **Spezielle Programme der Volkswagenstiftung:**

- Photonik (F. Caruso, H. Möhwald)
- Komplexe Systeme (G. Brezesinski, D. G. Kurth)

### • **Spezielle Programme des Bundesministeriums für Bildung und Forschung**

- Funktionale Supramolekulare Systeme (M. Antonietti, E. Donath, G. Sukhorukov)
- Bio-Nanotechnologie (F. Caruso, G. Sukhorukov)
- Synchrotron Forschung: Aufbau und Betreuung einer Beamline bei BESSY (W. Fenzl, Kooperation mit der Universität Potsdam, U. Pietsch)
- Neutronenstreuung: Betreuung eines Reflektometers am Hahn-Meitner-Institut Berlin (R. Krustev)

Des weiteren gibt es unter den zahlreichen Industriekon-takten zielgerichtete und konkret definierte Kooperationen mit Firmen wie Bayer, BASF, Beiersdorf, Capsulation, Clariant, Degussa, Firmenich, Henkel, L'oreal, Mitsubishi, Schering und Spiess-Urania.

## Internationale Kooperationen:

Neben dem internationalen Deutsch-Chinesischen Labor in Peking existieren unzählige internationale Forschungskon-takte, von denen hier die intensivsten und fruchtbarsten ge-nannt werden sollen:

- Europäische Zusammenarbeit über "From cell movement to biomimetic motile systems" im Rahmen des Human Frontier Science Programms, an der Forschergruppen von CNRS in Gif-sur-Yvette, dem Europäischen Institut für Onkologie in Mailand sowie dem Institut für molekulare Zellbiologie in Salzburg beteiligt sind.

- Deutsch-Französische Forschergruppe über "Komplexe Flüssigkeiten von 3D bis 2D", eine Kooperation mit CEA Saclay, der Universität Paris (Orsay), dem College de France, der Universität Toulouse, der Universität Montpellier und den Technischen Universitäten in München und Berlin
- Kooperation mit der Universität Bristol aufgrund der Verleihung des Max-Planck Preises an S. Mann
- INTAS Projekte mit der Akademie der Wissenschaften Moskau und wissenschaftlichen Gruppen in Kiew und Donetsk
- TMR Netzwerk über „Nanokapseln“, eine Kooperation mit der University Toulouse, der Universität Porto, der Ecole Normale Supérieure Paris, der Universität Genova und der Universität Wien

## Editorial Boards

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

- Advances in Coll. Surf. Sci. (R. Müller, Herausgeber)
- Chem. Phys. Mat. (H. Möhwald)
- Colloids and Surfaces (H. Möhwald, Herausgeber)
- Coll. Polym. Sci. (M. Antonietti)
- Current Opinion Coll. Interf. Sci. (H. Möhwald)
- European Physical Journal E (R. Lipowsky)
- Europhysics Letters (R. Lipowsky)
- Langmuir (H. Möhwald, M. Antonietti)
- Lecture Notes in Physics (R. Lipowsky)
- Macromolecular Journals of VCh (M. Antonietti)
- Nach.Chem.Lab.Tech. (M. Antonietti)
- Nano-Letters (H. Möhwald)
- New J.Chem. (M. Antonietti)
- New Rheol. J. (M. Antonietti)
- Prog. Polym. Sci. (M. Antonietti)
- Rev. Mol. Biotech. (M. Antonietti)

## Wissenschaftliche Beiräte:

- DECHEMA Arbeitsgruppe über "Chemische Nanotechnologie" (H. Möhwald)
- European Colloid and Interface Society (H. Möhwald, Präsident)
- Hahn-Meitner-Institut (H. Möhwald)
- Institute of Thin Films am FZ Jülich (H. Möhwald)
- Kolloid-Gesellschaft (H. Möhwald)
- Lower Saxonian University Evaluation Committee on Physics (H. Möhwald)
- Minerva Weizmann Committee (R. Lipowsky)
- Saxonian University development committee (H. Möhwald)

# Scientific Relations

## National Cooperations:

There are many national cooperations with universities and institutes. The most prominent ones in specialized areas are listed below, with responsible project leaders in brackets.

### • **Center of Excellence (SFB) on "Mesoscopic Composites"**

together with Potsdam University and all three universities of Berlin (M. Antonietti, H. Cölfen, D. G. Kurth, R. Lipowsky, H. Möhwald, H. Schlaad)

### • **Special Priority Programs**

each involving about 30 groups:

- Polyelectrolytes (G. Brezesinski, H. Dautzenberg, H. Möhwald, R. Netz, M. Schönhoff, C. Seidel)
- Wetting and Structure Formation (T. Fischer, R. Lipowsky, H. Riegler)
- Magnetic Fluids (F. Caruso, K. Landfester)
- Photonic Crystals (F. Caruso)
- Biomineralization (H. Cölfen)

### • **Special Programs of the VW-Foundation:**

- Photonics (F. Caruso, H. Möhwald)
- Complex Systems (G. Brezesinski, D. G. Kurth)

### • **Special Programs of the Technology Ministry:**

- Functional Supramolecular Systems (M. Antonietti, E. Donath, G. Sukhorukov)
- Bio-Nanotechnology (F. Caruso, G. Sukhorukov)
- Synchrotron Research: Coordination of beamlines (W. Fenzl) Commissioning of a beamline at BESSY (Cooperation with Potsdam University, U. Pietsch)
- Neutron scattering: Coordinated research at the reflectometer at the Hahn Meitner Institute Berlin (R. Krustev)

Among many industry contacts cooperations with well-defined targets have been with Bayer, BASF, Beiersdorf, Capsulution, Clariant, Degussa, Firmenich, Henkel, L'oreal, Mitsubishi, Schering, and Spiess-Urania.

## International Cooperations:

Beyond the International laboratory in Beijing described below there exist many international contacts, the most pronounced ones being:

- European Cooperation about "From cell movement to bio-mimetic motile systems" which is funded by the Human Frontier Science Program and includes research groups from CNRS in Gif-sur-Yvette, from the European Institute of Oncology in Milano and from the Institute of Molecular Cell Biology in Salzburg.

- German/French Collaborative Research Group on "Complex Fluids from 3D to 2D" with CEA Saclay, University Paris (Orsay), College de France, University Toulouse, University Montpellier and in Germany TU Munich and Berlin
- Cooperation with University Bristol through a Max-Planck Award to S. Mann
- INTAS projects with the Academy of Sciences Moscow and groups in Kiev and Donetsk
- TMR network on "nanocapsules" with University Toulouse, University Porto, Ecole Normale Superieur Paris, University Genova, University Wien

## Editorial Boards

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

- Colloids and Surfaces (H. Möhwald, editor)
- Coll.Polym.Sci. (M.Antonietti)
- Advances in Coll. Surf. Sci. (R. Miller, editor)
- Chem. Phys. Mat. (H. Möhwald)
- Current Opinion Coll. Interf. Sci. (H. Möhwald)
- European Physical Journal E (R. Lipowsky)
- Europhysics Letters (R. Lipowsky)
- Langmuir (H. Möhwald, M. Antonietti)
- Lecture Notes in Physics (R. Lipowsky)
- Macromolecular Journals of VCh (M. Antonietti)
- Nach.Chem.Lab.Tech. (M. Antonietti)
- Nano-Letters (H. Möhwald)
- New J.Chem. (M. Antonietti)
- New Rheol. J. (M. Antonietti)
- Prog.Polym.Sci. (M. Antonietti)
- Rev.Mol.Biotech. (M. Antonietti)

## Advisory Boards

- DECHEMA working group on "Chemical Nanotechnology" (H. Möhwald)
- European Colloid and Interface Society (H. Möhwald, president)
- Hahn Meitner Institute (H. Möhwald)
- Institute of Thin Films at FZ Jülich (H. Möhwald)
- Kolloid-Gesellschaft (H. Möhwald)
- Lower Saxonian university evaluation committee on physics (H. Möhwald)
- Minerva Weizmann Committee (R. Lipowsky)
- Saxonian University development committee (H. Möhwald)

# International Max Planck Research School on Biomimetic Systems

## Einleitung

Die Suche nach interdisziplinären Forschungsprojekten, die sowohl die Traditionalität als auch die Vielfalt der Bereiche Physik, Chemie und Biologie abdecken, nimmt beständig zu. Zukünftige Wissenschaftler müssen neue Aufgabenfelder mit fachübergreifender multidisziplinärer Ausbildung bewältigen, die den Lehrplan während ihres Universitätsstudiums vervollständigen und erweitern werden.

Um hervorragende Studenten aus der ganzen Welt anzuziehen und der Abwanderung von Wissenschaftlern in die USA („brain drain“) entgegenzuwirken, ist es nötig, unsere lokalen wissenschaftlichen Einrichtungen zu stärken und weltweit sichtbar zu machen. Dies kann nur geschehen, wenn jungen Wissenschaftlern eine hochwertige und exzellente Ausbildung geboten wird und ihnen Labore zur Verfügung gestellt werden, damit sie ihre Kenntnisse bestmöglich entwickeln und für eine erfolgreiche Karriere nutzen können.

Wir stehen heute einem wachsenden Interesse der Gesellschaft bezüglich der Zukunftsperspektiven, die durch wissenschaftliche Ergebnisse ermöglicht werden, gegenüber. Diese betreffen insbesondere Gebiete wie die Verbesserung der Lebensqualität (Gesundheit, Materialforschung usw.) und die nachhaltige Entwicklung.

Die „International Max Planck Research School on Biomimetic Systems“ vereint all diese Aspekte, indem sie begabten Studenten die Möglichkeit bietet, an hochaktuellen Forschungsthemen des interdisziplinären Gebietes der Biomimetik zu arbeiten. Die Schule organisiert Kurse, die von lokalen Wissenschaftlern und eingeladenen namhaften Vertretern aus der Physik, Chemie und Biologie durchgeführt werden. Mit diesem Kurssystem wird die Basis für eine erfolgreiche Karriere geschaffen.

Die „IMPRS“ ist ein Projekt der Max-Planck-Gesellschaft, das die internationale Bedeutung Deutschlands als Zentrum von Bildung und Forschung erhöhen und vor allen Dingen der Nachwuchsförderung dienen soll. Die insgesamt 29 „Research Schools“ sollen mit dazu beitragen, Deutschland in der Ausbildung von Studenten und Doktoranden unter die Ersten im internationalen Wettbewerb zu bringen, so dass wiederum die besten jungen Wissenschaftler für die eigene Arbeit gewonnen werden können.

Sprecher und Initiator der IMPRS on Biomimetic Systems ist Prof. Lipowsky, Direktor der Theorieabteilung am Max-Planck-Institut für Kolloid- und Grenzflächenforschung. Prof. Martin G. Peter, der den Lehrstuhl Naturstoffchemie am Institut für Chemie der Universität Potsdam innehat, hat die Funktion des Vize-Sprechers übernommen.

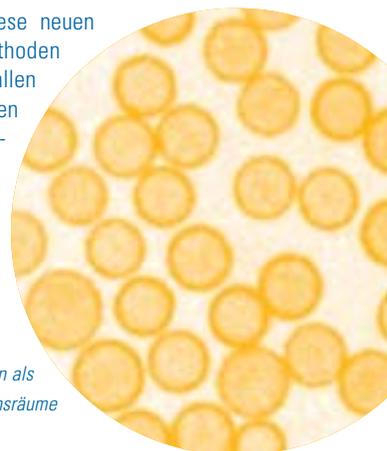
## Was sind Biomimetische Systeme?

Biomimetische Systeme sind Modellsysteme, durch die man die komplexe Selbstorganisation in der Biologie verstehen kann. Diese Forschungsweise basiert auf der Idee, experimentelle und theoretische Modelle zu entwickeln, die die biologischen Prozesse nachahmen.

Die projektbezogenen Themen der Schule decken eine Reihe von Systemen und Längenskalen ab, die von Nanostrukturen, wie Filamenten sowie molekularen Motoren über Mikrosysteme, wie Membranen, Vesikeln und Transportphänomenen bis hin zu Biomaterialien reichen. Der gegenwärtige Schwerpunkt der Schule liegt auf der Grundlagenforschung und dem Verstehen der charakteristischen Phänomene der einzelnen Ebenen und wie diese sich gegenseitig beeinflussen. Hinzu kommt, dass das Wissen angewendet werden kann, um biomimetische Materialien mit vorgegebenen physikalischen, chemischen und biologischen Eigenschaften zu entwerfen, die beispielsweise erforderlich sind für medizinische Anwendungen.

In Zukunft werden diese neuen mit biomimetischen Methoden gebauten Materialien auf allen Ebenen (Biokolloide, Zellen und Gewebe) mit den biologischen Systemen interagieren. Auf diese Weise schafft die Biomimetik die Grundlagen für die Entwicklung von Geweben und Implantaten.

*Polyelektrolyt-Hohlkapseln als biomimetische Reaktionsräume*



## Das Lehrangebot

Die „IMPRS on Biomimetic Systems“ wird vom Max-Planck-Institut für Kolloid- und Grenzflächenforschung unter Teilnahme aller Abteilungen in Zusammenarbeit mit drei Instituten der Universität Potsdam organisiert:

- Institut für Physik (Prof. J. Kurths)
- Institut für Chemie (Prof. M. G. Peter)
- Institut für Biologie und Biochemie (Prof. F. W. Scheller und Prof. D. Fürst)

Diese Zusammensetzung der Schule garantiert, dass alle nötigen Wissens Ebenen vorliegen, um die Komplexität der biologischen Systeme zu verstehen. Die Kurse, die von der Schule organisiert werden, umfassen daher Statistische Physik, Biophysik, Physikalische Chemie, Supramolekulare Chemie, Biochemie sowie Molekulare Zellbiologie. Ein Ziel des Lehrprogramms ist es, den Studenten eine fachübergreifende Ausbildung zu bieten. Darüber hinaus werden die Kurse so gestaltet, dass sie Studenten aus allen Disziplinen

zugänglich sind. Um Studenten aus aller Welt zu ermöglichen, die Kurse reibungslos zu besuchen, werden alle Veranstaltungen der IMPRS in englischer Sprache gehalten.

Die Kurse werden von lokalen und eingeladenen Wissenschaftlern durchgeführt und in zwei Kategorien eingeteilt. Die erste beinhaltet Kurse, die während des ganzen Semesters laufen und die den Studenten eher einen breiten Überblick über wichtige Basisdisziplinen oder Methoden geben. Dies ist ein dauerhafter Bestandteil jeden Jahresprogramms und umfasst im Jahr 2002/2003 folgende Bereiche:

- Theory of Soft- and Biomatter
- Colloidal Science and Biophysics
- Supramolecular Chemistry
- Numerical Simulations
- Molecular Cell Biology

Als zweite Kategorie gibt es Kompaktkurse, die typischerweise in einer begrenzten Anzahl von Vorträgen ablaufen. Sie decken einige spezielle Themen ab und können von Jahr zu Jahr wechseln, um Neues für interessierte Studenten anzubieten. Im Jahr 2002/2003 sind dies:

- NMR-Methods: Basics and Application to Colloidal Systems
- Colloids in Chemistry, Biology and Materials Science
- Numerical Analysis
- Biomimetic Materials
- Biomineralisation
- Organization of Cytoskeleton in Cells
- Physics of Polymers
- Theory of Protein Folding

Während die IMPRS-Studenten einige dieser Kurse erfolgreich belegt haben müssen, um ihr Studium zu vervollständigen, bestehen zudem große Bemühungen, alle anderen Studenten der Max-Planck-Institute und der Universität Potsdam mit einzubeziehen und zu ermuntern, daran teilzunehmen. Diesbezüglich wirkt die „IMPRS on Biomimetic Systems“ als einheitliche Einrichtung nicht nur zwischen den Disziplinen, sondern auch zwischen den Institutionen und Studenten.

Des Weiteren organisiert die IMPRS auch spezielle Veranstaltungen. So findet beispielsweise jedes Jahr ein Hauptsymposium statt, auf dem die Betreuer und Studenten ihre interdisziplinäre Arbeit innerhalb des gesamten Forschungsfeldes präsentieren. Um die Wirkung der Veranstaltungen zu erhöhen, werden oft externe Sprecher (auch aus dem Ausland) einbezogen, die typischerweise einen Hauptvortrag halten.

Außerdem wird ein- oder zweimal pro Jahr ein informelles Treffen aller IMPRS-Studenten organisiert, auf dem die Projekte kurz vorgestellt und verschiedene Themen von Interesse für die Studenten diskutiert werden.

## Die Studenten

Die Schule begann im Oktober 2000 mit ihren ersten Kursen und einer Anzahl von drei Studenten. Seit die ersten Bewerbungen eintrafen, wuchs die Zahl der Studenten sehr schnell an. Zurzeit gehören der „IMPRS on Biomimetic Systems“ 24 Studenten an, verteilt auf Labore der Universität Potsdam und des MPI. Sie sind aus einer sehr großen Anzahl von Bewerbungen aus aller Welt ausgewählt worden. Während des Jahres 2003 wird die erste Doktorarbeit abgeschlossen werden.

Gemäß Bestimmungen der Max-Planck-Gesellschaft wird mindestens die Hälfte der Stipendien bzw. Stellen an ausländische Staatsbürger vergeben und tatsächlich gibt es bislang nur sieben Studenten aus Deutschland an der IMPRS. Die anderen 17 kommen aus so verschiedenen Ländern wie Indien, Rumänien, Bulgarien, Algerien, Äthiopien, Polen, Brasilien, Italien, Indonesien und Russland.

An der „IMPRS on Biomimetic Systems“ erhalten alle Studenten entweder ein Stipendium vom MPI für Kolloid- und Grenzflächenforschung (mit einem Zuschuss der MPG) oder von der Universität Potsdam (mit Unterstützung des Landes Brandenburg). Darüber hinaus wird eine kleine Zahl von Studenten über externe Projekte (Drittmittel) finanziert.

Neue Studenten werden durch Bekanntgabe freier Stellen im Internet oder über Zeitschriften (wie zum Beispiel PhysicsWorld) angeworben. Dabei wird ein Bewerbungsschluss gesetzt, um die Auswahl auf einige Wochen zu konzentrieren. Zurzeit erhalten wir trotzdem während des ganzen Jahres konstant Bewerbungen.

## Informationen

Alle Aktivitäten der Schule finden Sie auf folgender Internetseite: [www.IMPRS.org](http://www.IMPRS.org). Potentielle Bewerber und Interessenten finden dort Informationen über das Kursangebot, einige Projektbeispiele und erhalten Zugang zu den Kontaktadressen und Bewerbungsbedingungen.

Für IMPRS Studenten und alle anderen interessierten Wissenschaftler der Max-Planck-Institute und der Universität Potsdam sind auf der Website die Zeitpläne für die Kurse sowie Links zu den Webseiten der einzelnen Dozenten zu finden.

Das Internet und das Email-System ist die wichtigste Form der Kommunikation innerhalb der Schule, da die Abteilungen der Universität und des Max-Planck-Institutes an verschiedenen Orten sind.

Angelo Valleriani  
Koordinator der „IMPRS on Biomimetic Systems“

# International Max Planck Research School on Biomimetic Systems

## Introduction

There is an increasing quest for interdisciplinary research projects covering fields traditionally as diverse as physics, chemistry and biology. Future researchers will have to cope with it by means of a multidisciplinary education which transcends and completes the curriculum offered during their University studies.

There is also a need to attract excellent students from all around the world and counter the brain-drain to the USA in order to strengthen our local research institutions and to increase their visibility in the global landscape. This can only be done by offering young researchers a high-profile education and laboratory support, where they can best develop their skill and invest for a successful career.

We face also an increased attention from side of the Society towards the future perspectives offered by scientific results, especially in fields related to the improvement of quality of life (e.g. health issues, materials sciences etc.) and sustainable development.

The International Max Planck Research School on Biomimetic Systems addresses all these points by offering talented students the possibility to work on cutting-edge research topics in the interdisciplinary field of biomimetics, and by organizing courses, held by local and renowned invited scientists from physics, chemistry and biology, which constitute the backbone of a prestigious curriculum.

This Graduate School is a project of the Max Planck Society to raise Germany's international prominence as a center of research and education. The aim of the 29 Research Schools is also to contribute to positioning Germany in the top flight in graduate and Ph.D. student's education in international competition for the best young scientists.

Speaker and initiator of the IMPRS on Biomimetic Systems is Prof. Lipowsky, who is director of the Theory Division of the Max Planck Institute of Colloids and Interfaces. Vice-speaker is Prof. Martin G. Peter, chair of Chemistry of Natural Products of the Institute of Chemistry at the University of Potsdam.

## What are Biomimetic Systems?

These are model systems by which one can understand the complex self-organization in biology. This approach is based on the idea of defining experimental and theoretical models that imitate the way nature works.

The main topics of the projects of the school cover a set of systems and length scales ranging from nanostructures like filaments and molecular motors, to microsystems like membranes, vesicles and transport phenomena up to biomaterials. The present focus of the school is on basic research, on understanding the phenomena characteristic for each level and how these levels interact with each other. In a second step, this knowledge may be used to construct biomimetic materials with predefined physical, chemical and biological properties such as those required for instance for medical applications.

In the future then, the new materials constructed using the biomimetic approach will interact with their biological counterparts at all levels (biocolloids, cells and tissues). In this way, biomimetics provides the knowledge base for cell and tissue engineering.

## The Curriculum

The IMPRS on Biomimetic Systems is organized by the Max Planck Institute of Colloids and Interfaces with the participation of all its departments, in collaboration with three institutes of the University of Potsdam:

- Institute of Physics (Prof. J. Kurths)
- Institute of Chemistry (Prof. M. G. Peter)
- Institute of Biology and Biochemistry (Prof. F. W. Scheller and Prof. D. Fürst)

This composition of the school guarantees that all levels of knowledge necessary to address the complexity of biological systems are present. These include statistical physics, biophysics, physical chemistry, supramolecular chemistry, biochemistry and molecular cell biology. This is also reflected in the kind of courses that are organized by the school.

As stated in the introduction, one aim of the curriculum is to offer the students a multidisciplinary education and therefore a certain effort has been devoted to design courses accessible to students from all disciplines. Moreover, in order to allow students from all around the world to attend all activities, all lectures of the IMPRS are given in English.



The courses are given by local and invited scientists and are organized in two categories. In the first category there are the Semester Courses which run over a whole semester. These are courses meant to give students a rather broad view of important basic disciplines or methods and therefore are a stable component of each year's program. In the year 2002/2003 these are:

- Theory of Soft- and Biomatter
- Colloidal Science and Biophysics
- Supramolecular Chemistry
- Numerical Simulations
- Molecular Cell Biology

In the second category there are Compact Courses which typically run for a limited number of lectures. They cover some special topic and may change from one year to the next in order to offer always something new to the interested students. In the year 2002/2003 these are:

- NMR-Methods: Basics and Application to Colloidal Systems
- Colloids in Chemistry, Biology and Materials Science
- Numerical Analysis
- Biomimetic Materials
- Biomineralisation
- Organization of Cytoskeleton in Cells
- Physics of Polymers
- Theory of Protein Folding

On the one hand the IMPRS students have to successfully follow some of these courses in order to complete their doctoral studies, on the other hand a strong effort is made to involve all other students of the Max Planck Institute and of the University of Potsdam and to encourage them to attend. In this respect, the IMPRS on Biomimetic Systems is acting as a unifying entity not only among disciplines but also among institutions and students.

Beside courses, the IMPRS organizes also special events. Every year there is at least one general symposium where supervisors and students from all disciplines present their work to the whole scientific community around the school. To increase also the impact of these meetings, there are often also external speakers (sometimes from abroad) who typically deliver a plenary lecture.

Moreover, there is an informal meeting of all IMPRS-Students organized once or twice every year where the projects are briefly introduced and several other issues of interest for the students are discussed.

## The Students

The school started in October 2000 with the first courses and three students. As applications were arriving, the number of students grew very fast. At present the IMPRS on Biomimetic Systems counts 24 students distributed among the laboratories of the University and of the Max Planck Institute. They have been selected out of a large number of applications from all around the world. During the year 2003 we expect the first Ph.D. to be issued.

According to the rules set out by the Max Planck Society, at least half of the fellowships available should be reserved to non-German citizens and indeed only 7 come from Germany. The other 17 come from countries as diverse as India, Rumania, Bulgaria, Algeria, Ethiopia, Poland, Brazil, Italy, Indonesia and Russia.

At the IMPRS on Biomimetic Systems all students receive a stipend either from the Max Planck Institute (with the support of the Max Planck Society) or from the University of Potsdam (with the support of the State of Brandenburg). A small number of students are also financed through external projects.

New students are typically recruited after some publicity for open positions is made on the internet or in some key journals (like for instance PhysicsWorld) and a deadline is set in order to concentrate the selection in few weeks time. Nevertheless, we are now in a situation where applications arrive at a constant pace during the whole year.

## Information

All activities of the school are posted in a dedicated web page [www.IMPRS.org](http://www.IMPRS.org), set out in order to be easy to remember and to access. Therein possible applicants can find the information about the courses offered, some examples of projects and the necessary addresses and requirements for an application.

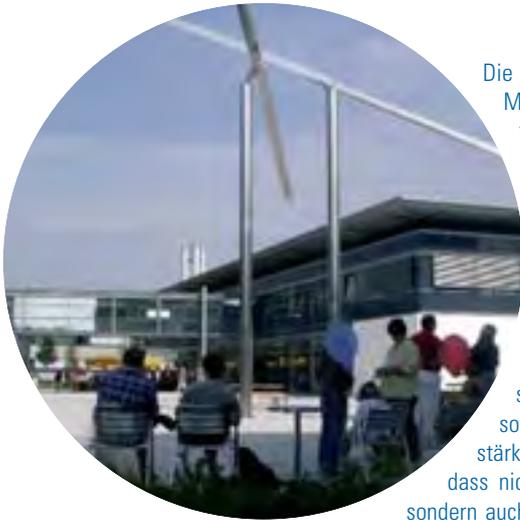
For IMPRS-Students and for all other interested scientists at the Max Planck Institute and at the University of Potsdam, the web page is the place where they find the timetable of the courses and links to the web pages of the lecturers.

The internet and email system is the most important form of communication inside the school, given that the departments of the University and the Max Planck Institute are not all in the same place.

Angelo Valleriani  
Coordinator of the IMPRS on Biomimetic Systems



## Presse- und Öffentlichkeitsarbeit



Die Presse- und Öffentlichkeitsarbeit am Max-Planck-Institut für Kolloid- und Grenzflächenforschung sieht sich vorrangig als Schnittstelle zwischen Wissenschaft und Gesellschaft. Ein Hauptziel ist es, unsere aktuelle Forschung in das Bewusstsein der allgemeinen Öffentlichkeit, der Politik, der Presse, unserer Kooperationspartner, zukünftiger Studenten, ehemaliger Institutsangehöriger sowie der internen Gemeinschaft zu bringen und ihre Akzeptanz sowie Anerkennung in der Gesellschaft zu stärken. Für uns ist es von großer Bedeutung, dass nicht nur „eingeweihte“ Wissenschaftler,

sondern auch jeder, der sich für moderne Forschung interessiert, die Möglichkeit bekommt, sich über die Ziele des Instituts zu informieren.

Um dies gewährleisten zu können, organisieren wir Institutsführungen sowie Vorträge an Schulen und veröffentlichten Broschüren, wie den vorliegenden Zweijahresbericht, den wir Ihnen auf Anfrage gern zusenden. Des Weiteren sind wir bemüht, Ihnen jegliche Unterstützung bei auftretenden Fragen zu bieten. Einer unserer jährlichen Höhepunkte ist der „Tag der offenen Türen“ im Wissenschaftspark Golm, der interessierten Besuchern aller Altersklassen einen faszinierenden und mitunter auch vergnüglichen Einblick in die umfangreiche wissenschaftliche Arbeit unseres Instituts bietet. Im Jahr 2003 wird der „Tag der offenen Türen“ am 30. August stattfinden. Das mannigfaltige Programm mit Institutsführungen, Experimenten, Vorträgen und Mitmach-Aktionen bietet Jung und Alt Wissenschaft zum Anfassen und die Möglichkeit High-Tech-Technologien hautnah zu erleben.

Darüber hinaus stellt die Verbreitung der aktuellsten wissenschaftlicher Ergebnisse in Zeitungen, im Fernsehen und im Radio eine wichtige Aufgabe der Presse- und Öffentlichkeitsarbeit dar. Mit der Herausgabe von Pressemitteilungen wollen wir die Aufmerksamkeit der Gesellschaft auf die Bedeutung der Grundlagenforschung im Allgemeinen und der zukünftigen Entwicklungen in der Kolloid- und Grenzflächenforschung im Besonderen richten. Ein besonderes Anliegen dabei ist es zu zeigen, dass die Welt der Wissenschaft und Technologie faszinierend, aufregend, abwechslungsreich und lohnend ist. Informieren Sie sich in der vorliegenden Broschüre über neueste wissenschaftliche Ergebnisse und finden Sie einen grundlegenden Einblick in die Forschung des Instituts für Kolloid- und Grenzflächenforschung.

Katja Schulze



## Public Relations

Public relations at the Max Planck Institute of Colloids and Interfaces serve as the interface between the scientists' work and the public. We want to 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.

To pursue this task, tours through the institute as well as talks at schools are organized, brochures – such as the biannual report are published and distributed on request, and informal support is provided whenever necessary. One of our highlights every year is the "Open Day" on the Research Campus Golm, which is an interesting and fun-packed day, combining demonstrations of high-tech learning facilities with hands on activities for all age groups. This year's Open Day will be held on August 30. There will be lab tours, popular talks and scientific demonstrations providing an excellent opportunity for everybody to experience scientific activity at first hand.

Another main objective is the distribution of the most interesting results to an audience beyond the scientific community by stimulating media coverage in newspapers, TV and radio.

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

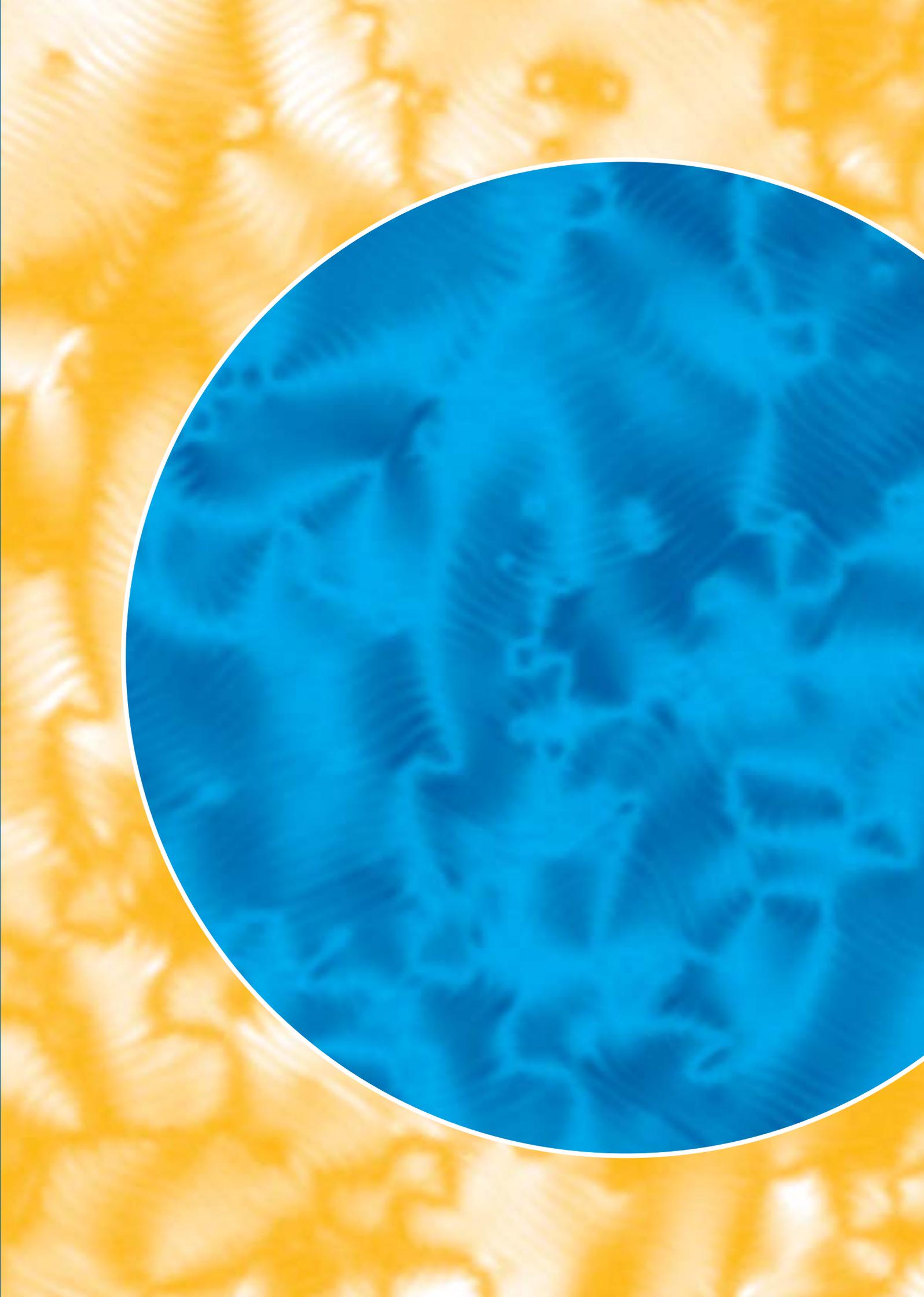
Katja Schulze





COLLOID  
CHEMISTRY

COLLOID CHEMISTRY



# Research in the Department of Colloid Chemistry

## Scientific Profile

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

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

In the time of this report, Karl-Heinz Goebel, Herbert Dautzenberg (retirement), Rachel Caruso (Melbourne) and Hans-Peter Hentze (Newark) left the department, while three new groups, headed by Hans-Börner, Charl Faul and Markus Niederberger, have been established. This turnover is rather typical and keeps the department dynamic.

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

In detail, the following topics are treated by the department:

- Heterophase Polymerization
- Polyelectrolytes and their Complexes
- Amphiphilic Polymers
- Mesoporous Materials
- Modern Techniques of Colloid Analysis

## Heterophase Polymerization

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

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

- to gain a better understanding of the nucleation period and particle formation. For this purpose, new experimental online multidetection techniques are developed and supplemented by theoretical approaches (Dr. Klaus Tauer).

- to simplify the synthesis of complex polymer molecules (e.g. block & graft copolymers) and colloids (e.g. core-shell lattices, reinforced materials) by emulsion polymerization and rational use of the particle interfaces (Dr. Klaus Tauer).
- Inisurfs and Surfmers, and new stabilizers for better polymer dispersions (Dr. Klaus Tauer).
- Miniemulsion polymerization allows the formulation of very small polymer lattices by high shear treatment of dispersions. Since one polymerizes preformed oil droplets under preservation of droplet number, composition, and inner structure, miniemulsion polymerization significantly extends the possibilities of emulsion polymerization. (Dr. Katharina Landfester).
- Synthesis of organic/inorganic hybrids by encapsulation of inorganic colloids or magnetic particles using miniemulsions. Those particles have strong impact in diagnostics and magnetotherapy (Dr. Katharina Landfester, within a DFG-Schwerpunkt).
- Single Molecule Chemistry on Polymers and confined crystallization in miniemulsion droplets Physical or chemical procedures are performed in a molecule-per-molecule fashion. Examples for this are complex reactions or folding/crystallization of polymers or proteins in the absence of any intermolecularity. (K. Landfester, Markus Antonietti)

## Polyelectrolytes and their Complexes

Polyelectrolytes are water soluble and combine sustainability with a broad spectrum of properties. Polyelectrolytes can be found in many aspects of daily life, such as thickeners, diapers or in waste water treatment. Our research is focused on the basic understanding of diverse polyelectrolyte properties and modern derivatives of polyelectrolytes:

- Polyelectrolyte/polyelectrolyte complexes and polyelectrolyte/surfactant complexes offer a wide range of structured materials, the diversity of which is far from being fully explored. Our work is focused on the construction of nanostructures with astonishing complexity. Due to their simple synthesis (common precipitation from water) and the commercial starting materials, they represent the cheapest polymer liquid crystals. Such complexes can exhibit selective gas permeation or ultra-low surface energies. Current work extends this Ionic Self Assembly (ISA) towards inorganic polymers, dyes, and biological tectons (Dr. Charl Faul).

## Amphiphilic Polymers

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

- The micelle formation and lyotropic liquid crystalline phase behavior of amphiphilic polymers is examined in dependence of molecular parameters as well as the amount of solubilized material (Dr. Helmut Schlaad).
- The introduction of secondary interactions such as H-bridges, dipole interactions or metal-ligand binding results



in superstructures with more complex order (Dr. Helmut Schlaad).

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

### Mesoporous Materials by Nanocasting and Nanocoating

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

- the use of polymer gels, fiber, membranes and beads to create structures and shaped objects made from nanoparticles by nanocasting and nanocoating (Dr. Markus Niederberger)
- the employment of these structures as supports for designer catalysts where nanoparticle formation is a integer part of the nanostructure set-up and profitably controlled by either the porogens or the pore geometry (Dr. Markus Niederberger, the "Zeit-Project" together with the Fritz Haber Institute)
- the synthesis of new well defined nanoparticles with function by solvent and ligand assisted synthetic pathways and their self-assembly into organized 3D superstructures by ligand encoding (Dr. Markus Niederberger)
- the use of nanocasting as an analytical tool, i.e. to characterize fragile soft matter superstructures, such as the worm-like assemblies of cyclodextrines or other supra-molecular entities (Markus Antonietti)

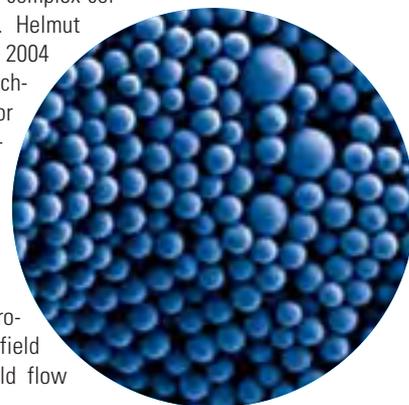
- implementation of experiments within the pore system for "nanochemistry", i.e. the analysis of specific effects of a nanoconfinement on a physical properties and chemical reactions (Markus Antonietti)



### Modern Techniques of Colloid Analysis

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

- the development of new ultracentrifugation techniques. Together with industry, a multidetection kit for the ultracentrifuge is developed, e.g. coupling the separation with Raman-, UV- or fluorescence detection. This would allow an in-situ chemical analysis within a separating complex colloidal mixture and revitalize the AUC. (Dr. Helmut Cölfen, Project Analytical Ultracentrifugation 2004 together with the BASF AG). New gradient techniques for the AUC such as pH-, chirality- or enzymatic activity gradients reveal new information about complex spatio-temporal phenomena (Dr. Helmut Cölfen).
- special techniques of transmission and scanning electron microscopy on soft, structured matter (Dr. Jürgen Hartmann)
- the improvement of diverse techniques of hydrodynamic chromatography such as thermal field flow fractionation and asymmetric flow field flow fractionation (Dr. Helmut Cölfen)
- computational analysis of high precision static light scattering experiments (Dr. Gudrun Rother)
- exploratory research for the application of new techniques of dynamic light scattering to colloidal systems, e.g. using optical near fields or the "ellipsometric light scattering". (Dr. Reinhard Sigel)



### Larger Equipment and Central Service Labs of the Department

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

Two of the labs, the electron microscopy and the X-ray lab, are so-called "central service labs", i.e. they belong and are operated by the department, but are designated to perform scientific routine measurements for the whole institute.

Prof. Markus Antonietti  
Director of the Department of Colloid Chemistry

## Miniemulsions



### What Are Miniemulsions?

Miniemulsions are dispersions of critically stabilized oil droplets with a size between 50 and 500 nm prepared by shearing a system containing oil, water, a surfactant and a hydrophobe. Polymerizations in such miniemulsions, when carefully prepared, result in latex particles which have about the same size as the initial droplets. This means that the appropriate

formulation of a miniemulsion suppresses coalescence of droplets or Ostwald ripening. The polymerization of miniemulsions extends the possibilities of the widely applied emulsion polymerization and provides advantages with respect to copolymerization reactions of monomers with different polarity, incorporation of hydrophobic materials or with respect to the stability of the formed latexes.

### Polyurethane Dispersions

Polyurethane latexes can be made by direct miniemulsification of a monomer mixture of diisocyanate and diol in an aqueous surfactant solution followed by heating (Fig. 1). This is somewhat special since one might expect a suppression of the polyaddition by side reactions between the very reactive diisocyanates and the continuous phase water. However, polymer dispersions with high molecular weight polymer were obtained after optimizing the reaction parameters.

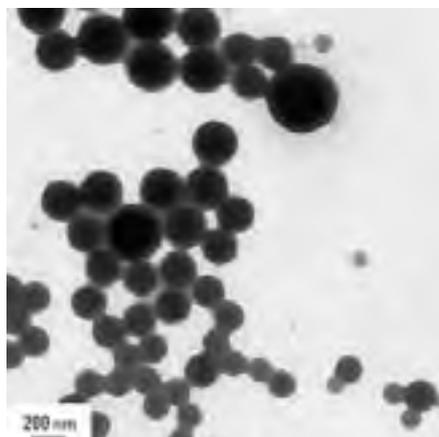


Fig. 1: Polyurethane latex obtained by polyaddition in miniemulsion

### Polyester Dispersions

Hydrophobic polyesters have been synthesized in miniemulsion in the presence of large amounts of water. The yield of the esterification and the molecular weight of the polyester have been determined for different reaction conditions. Important parameters are the water concentration inside the particles and the structure of the alcohol monomer. Alcohol compounds bearing electron-donating groups allow displacing the equilibrium toward ester formation. It was also shown that polyester/polystyrene hybrid particles can be synthesized in a very simple way using a one pot procedure.

### Amphiphilic Copolymers

The polymerization process of two monomers with different polarities was carried out in direct or inverse miniemulsions using the monomer systems of different hydrophilicity. The monomer, which is insoluble in the continuous phase, was miniemulsified in the continuous phase in order to form stable and small droplets. The monomer with the opposite hydrophilicity dissolves in the continuous phase. Starting from those two dispersion situations, the locus of initiation (in one of the two phases or at the interface) was found to have a great influence on the reaction products and the quality of the obtained copolymers (Fig. 2).

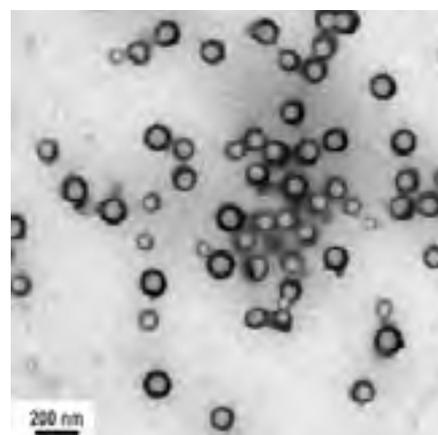


Fig. 2: Acrylamide/methyl methacrylate copolymer particles obtained in a direct miniemulsion polymerization with interfacial initiation

### Chitosan Stabilized Polymer Dispersions, Capsules and Chitosan Grafting Products

The potential of chitosan as an emulsion stabilizer was combined with the miniemulsion technique to generate oil droplets, hollow capsules, and latex particles in the diameter range of 100 nm to 300 nm carrying a functional biopolymer surface. The addition of biocompatible costabilizers with higher flexibility either to the oil phase or the water phase, allowed making very small nanocapsules of biopolymer hybrids (Fig. 3).

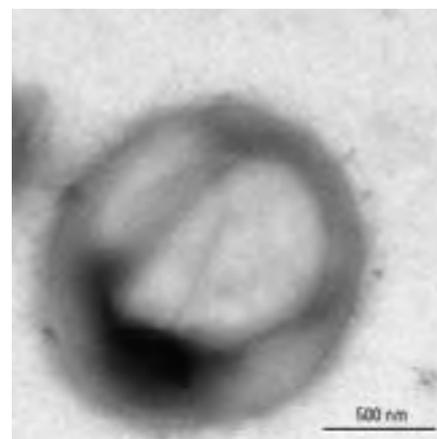


Fig. 3: Capsule preparation using chitosan as biocompatible stabilizer

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### Fluorinated Latexes

Fluorinated latexes in the size range of 100 to 250 nm were made by the polymerization of miniemulsions of fluoroalkyl acrylates as fluorinated monomers under employment of rather low doses of protonated surfactants. In addition, it was shown that miniemulsification of mixed monomer species allows efficient copolymerization reactions to be performed with standard hydrophobic and hydrophilic monomers in a joint heterophase situation, resulting either in core-shell latexes or in statistical copolymers (Fig. 4). Contrary to the pure fluorinated polymers, those copolymers dissolve in organic solvents but still show the profitable interface properties of the fluorinated species.

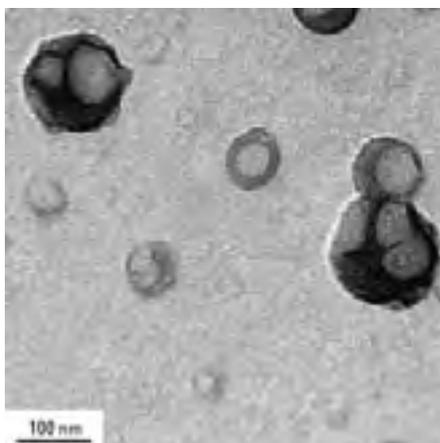


Fig. 4: Copolymer particles consisting of fluorinated and protonated acrylates

### Encapsulation of Magnetite Particles

The encapsulation of high amounts of magnetite into polystyrene particles could efficiently be achieved by a new three-step preparation route including two miniemulsion processes. Characterization by thermogravimetry, preparative ultracentrifugation, and transmission electron microscopy showed that up to 40 % magnetite could be encapsulated resulting in particles with a high homogeneity of the magnetite content (Fig. 5). Magnetometry measurements revealed that the included iron oxide aggregates still consisted of separated superparamagnetic magnetite particles.

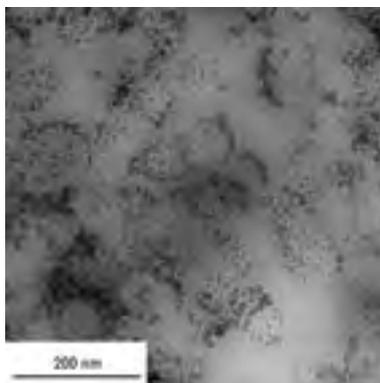


Fig. 5: Encapsulation of magnetite in polystyrene

### Semiconducting Polymer Spheres

Layers of conjugated semiconducting polymers could be deposited from aqueous dispersion prepared by the miniemulsion process (Fig. 6). Dispersions of particles of different conjugated semiconducting polymers could be prepared with well controllable particle sizes ranging between 70 to 250 nm by using a miniemulsion process. The concept of semiconducting polymer nanoparticles also allowed to form multilayer structures by e.g. depositing a first layer from a solution of a polymer and overcoated it by semiconducting polymer nanospheres of the second polymer from an aqueous phase, followed by annealing and film formation.

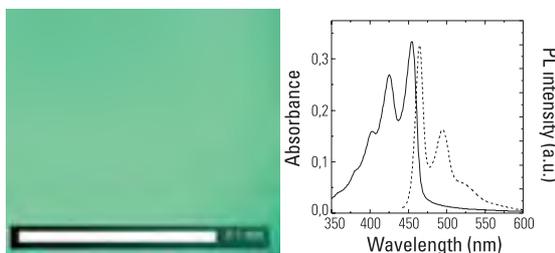


Fig. 6: a) Photoluminescence micrograph of a layer deposited from a semiconducting nanoparticle dispersion. b) Absorption and photoluminescence spectrum of the layer in a).

### Crystallization in Miniemulsion Droplets

Crystallization in miniemulsion droplets was shown to be strongly influenced due to the infinite size of the droplets. It was shown that the temperature of crystallization in miniemulsion droplets is significantly decreased as compared to the bulk material. This could be attributed to a very effective suppression of heterogeneous nucleation. In some case, the confinement in small droplets changed, e.g. in even alkanes the crystal structure changed from a triclinic (in bulk) to an orthorhombic structure.

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### References:

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## Heterophase Polymerization



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polymerization of vinyl chlorid

**Since 1992:** Group Leader  
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Heterophase polymerization techniques are a fascinating and attractive example of applied polymer colloid chemistry. Our main research topics of the last two years were (a) exploration of new ways to prepare block copolymers by radical heterophase polymerization, (b) mechanistic investigation of controlled radical polymerization with 1,1-diphenylethylene (DPE) based precursor polymers, (c) further evaluation of poly(ethylene glycol)-azo-initiators, and (d) development of procedures to prepare  $\mu\text{m}$ -sized, monodisperse particles with surface poly(ethylene glycol) groups.

### Preparation of Block Copolymers

The strategy employed consists of a multi-stage radical heterophase polymerization by utilizing the ceric ion redox initiation mechanism to generate radicals at preferably hydroxyl group substituted polymer chain ends that subsequently form polymeric micelles or particles during an aqueous heterophase polymerization as isolated reaction loci where the further block copolymer formation takes place after addition of another batch of monomer. This strategy allows the preparation of very unique block copolymers, which are not accessible by any other route. Examples are poly(ethylene glycol)-*b*-poly(N-isopropyl acrylamide)-*b*-poly(acrylamidopropane sulfonate), polystyrene-*b*-poly(N-isopropyl acrylamide)-*b*-poly(styrene sulfonate), or poly(styrene sulfonate)-*b*-poly(methacrylic acid) [1]. Besides the chemical distribution the block copolymer nanoparticles possess at least under wet conditions (in the dispersed state) also a characteristic density distribution which changes upon electrolyte addition and/or temperature changes. Moreover, particles of this kind exhibit interesting features which are not yet completely understood. For example, transmission electron microscopy (TEM) images of poly(ethylene glycol)-*b*-poly(N-isopropyl acrylamide)-*b*-poly(methyl methacrylate) (PEG-PNIPAM-PMMA) triblock copolymer particles show a hairy morphology whereas atomic force microscopy (AFM) images reveal a rather tubelike morphology (Fig. 1). This polymerization strategy can also be used to prepare block copolymer particles with special core morphology such as PEG-*b*-PNIPAM-*b*-poly(styrene sulfonate) particles where the core consists of cross-linked poly(styrene sulfonate). These hydrophilic gel particles have been used to prepare redispersible polyelectrolyte surfactant complexes that are colloidal particles with anisotropic, crystalline cores. Fig. 2 shows a TEM picture of cross sections of such colloidal complexes with tetradecyltrimethyl ammonium counterions [2].

### Control of Radical Polymerizations with DPE Precursor Polymers

Recently it was found that the use of (DPE) in conventional free radical polymerization allows a high degree of structural control [3]. The principle of this new method consists of a two-step polymerization. In the first step a DPE-containing precursor polymer is prepared, which in a second polymerization

leads to the formation of block copolymers. The two steps can be carried out either sequentially and spatially separated or conducted like a one pot synthesis with consecutive addition of monomers. In contrast with all other methods of controlled radical polymerization, the DPE-based technique can be applied for all types of acrylate, methacrylate, vinyl and styrene monomers. Moreover, it can be applied in bulk, solution as well as heterophase polymerizations and the DPE-precursor polymer can be either hydrophilic or hydrophobic. In collaboration with the BASF Coatings AG the mechanism of this reaction was investigated. It turned out that the active species in the precursor polymer is the  $\alpha$ ,  $\beta$ -dimer unit which is formed by combination termination of two DPE-ended radicals (Formula 1) [4, 5]. The results of comprehensive studies reveal that the semiquinoid structure of the precursor polymer is activated by the attack of free radicals and thus, in a second stage polymerization with a second monomer, block copolymers are formed. The block copolymer yield can be well above 90 % but depends strongly on the ratio between the amount of DPE-containing precursor polymer and the initiator and monomer concentration used in the second stage (Fig. 3). The mechanism proposed is able to explain at least qualitatively all experimental results including the restriction of this mode of control of radical polymerization to the formation of diblock copolymers only.

### Poly(Ethylene Glycol)-Azo-Initiators in Heterophase Polymerizations

The use of nonionic poly(ethylene glycol)-azo-initiators (cf. Formula 2) instead of ionic initiators in emulsion polymerizations offers interesting possibilities to modify colloidal and polymeric properties of polymer dispersions. Experimental results have been obtained for various kinds of anionic, cationic, and nonionic stabilizers. For example, in a styrene emulsion polymerization with monomer to water mass ratio of 1:4 at a given concentration of 1 % with respect to monomer mass of either an anionic or a cationic surfactant the replacement of either peroxydisulfate or 2,2'-azobis(2-amidinopropane)-dihydrochloride, respectively, by PEGA200 leads to particles with considerably smaller size, polymers with higher molecular weight, and latexes with higher viscosity. These results indicate on the one hand a special interaction between the PEG-radicals and ionic surfactant and on the other hand the influence of the ionic strength on aqueous heterophase polymerization [6].

### Large, Monodisperse Poly(Ethylene Glycol) – Coated Latex Particles

Polymer particles with polar functional groups such as poly(ethylene glycol) on the surface are widely utilized in biomedical applications particularly for protein immobilization and cell adhesion studies. Depending on the size and morphology, the particles prepared are also considered to be useful for use as size-exclusion and HPLC packings. The objective of this project was to develop synthetic routes to prepare large monodisperse particles with a PEG shell. For

this the following synthesis strategy was developed which is illustrated in **Fig. 4** by means of scanning electron microscopy (SEM) and light microscopy (LM) images. First, polystyrene seed particles have been prepared by dispersion polymerization in ethanol – water mixtures with poly(vinyl pyrrolidone) as stabilizer and 2,2'-azobisisobutyronitrile as initiator. These particles have been swollen with a large excess of styrene by activated swelling procedures (step A in **Fig. 4**) and subsequently polymerized (step B in **Fig. 4**). Finally, these particles were used as seed in a second seed copolymerization with styrene/PEG-mono methyl methacrylate with average molecular weights of PEG chains of 1000 g mol<sup>-1</sup> and 4000 g mol<sup>-1</sup> as monomer mixture and PEGA200 (**Formula 2**) as initiator (step C in **Fig. 4**). The developed strategy allows the preparation of monodisperse polystyrene particles with PEG shells in the size range between 1 and 10 μm [7-9].

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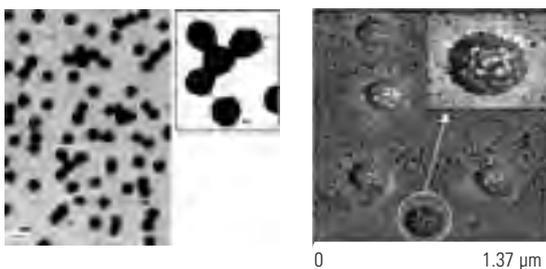


Fig. 1: TEM (left) and AFM image (right) of PEG-PNIPAM-PMMA triblock copolymer particles; the bar indicates 200 nm

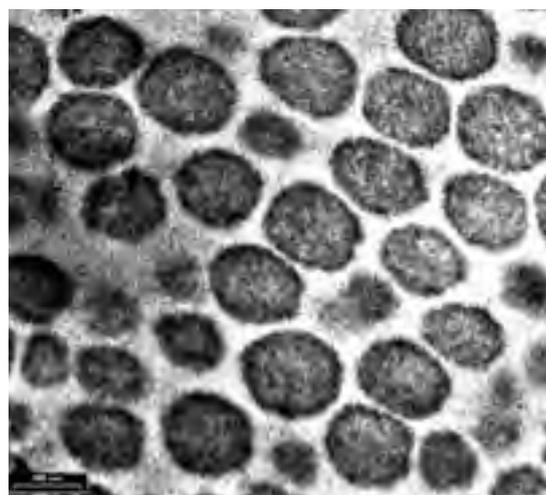
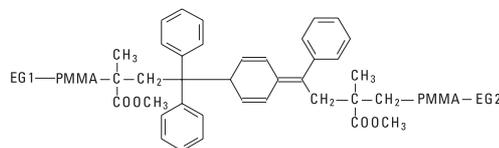


Fig. 2: TEM picture of cross section of polyelectrolyte surfactant complex particles; the bar indicates 300 nm



Formula 1: Active semiquinoid structural unit ( $\alpha,\beta$ -dimer) in DPE – PMMA precursor polymers; EG1 and EG2 denote different end groups arising from initiating radicals

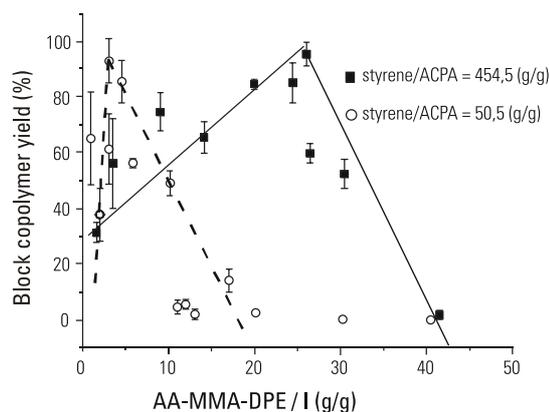
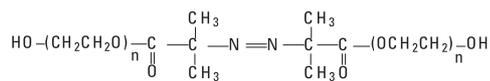


Fig. 3: Block copolymer yield between a hydrophilic precursor polymer made of acrylic acid, methyl methacrylate and DPE (AA-MMA-DPE) and styrene during an aqueous heterophase polymerization with 4,4'-azobis(4-cyanopentanoic acid) (ACPA) as initiator (I) in dependence on the precursor polymer to initiator ratio for two different monomer to initiator ratios (each experiment was repeated four times; lines are just for guiding the eyes)



Formula 2: Poly(ethylene glycol)-azo initiators (PEGA) (PEGA200 n-4.5)

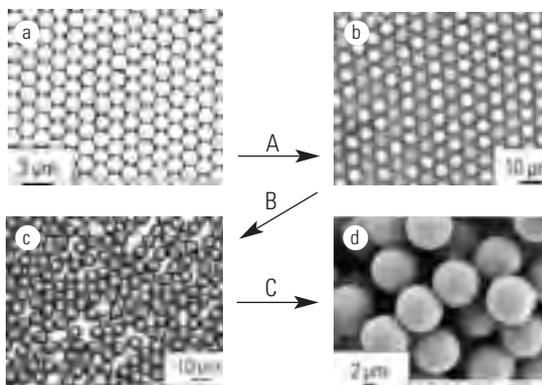


Fig. 4: Images of monodisperse polymer particles: a – SEM of seed particles (polystyrene), b – LM of swollen seed particles (styrene + polystyrene), c – LM of polymerized swollen particles (polystyrene), d – SEM of composite particles PS/P(S-PEGMMA)

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# POLYELECTROLYTES AND THEIR COMPLEXES

## Ionic Self-Assembly: Facile Route for the Production of Functional Nanostructured Materials



In the field of supramolecular chemistry a variety of noncovalent synthesis strategies or approaches e.g. hydrogen bonding, charge-transfer interactions, electrostatic interactions, have been established over the last few years to organize matter on a molecular level. Recently, we introduced a new, facile synthesis strategy, so-called ionic self-assembly (ISA).

ISA makes use of electrostatic interactions between charged surfactants and oppositely charged oligoelectrolytic species to direct the molecular assembly of these tectonic units into highly organized arrays (Fig. 1).

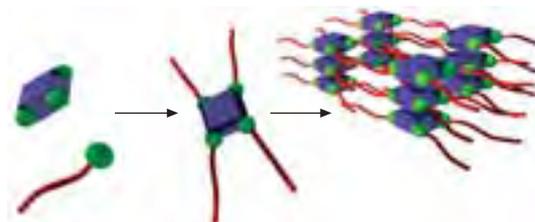


Fig. 1: Schematic representation of the ISA process

In initial investigations into the ISA process [1] supramolecular complexes were synthesized from commercially available azobenzene dyes and a series of alkylammonium surfactants. In order to ascertain the binding behavior of such complexes, binding isotherms were calculated from titration data obtained with a surfactant-selective electrode. This showed that the binding process was indeed cooperative and exhibited, similar to polyelectrolyte-surfactant complexes, a critical aggregation concentration.

The resulting complexes produced materials that exhibited either gel-like or crystalline needlelike morphologies. The crystalline materials show a very high degree of pleochroism, with dichroic rates over 40, i.e. the single azo-dye tectons are perfectly aligned over larger distances.

Detailed investigations [2] of the structures of such complexes showed that the morphology of these nanostructured complexes could be tuned through careful choice of the starting materials. Through variation of the charge substitution pattern on the azodyes, as well as changing the length and number of the alkyl tails of the amphiphile, highly ordered crystalline or thermotropic liquid-crystalline materials were accessible (Fig. 2).

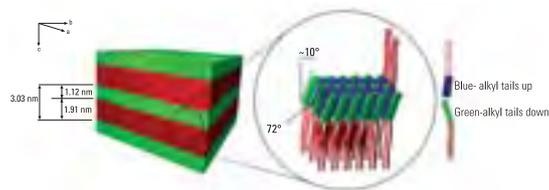
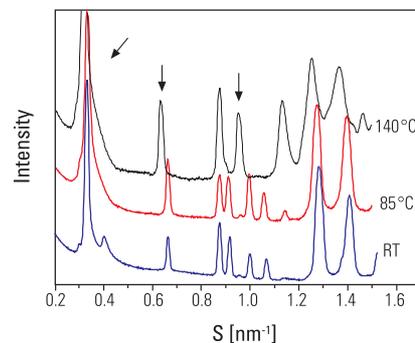


Fig. 2: Small-Angle X-ray Scattering Diffractogram and structure proposal for a highly ordered crystalline dye-surfactant complex

In an effort to extend and generalise the ISA concept [3] a variety of other oligoelectrolytic materials were also employed as tectonic units. This provides the opportunity to include not only shape-rigid organic tectons into the 'molecular toolbox' available for construction of nanostructured materials, but also shape-rigid inorganic tectons, as well as more complicated functional organic tectons. These will be discussed briefly below.

### Functional Organic Tectons:

#### Perylenediimide-surfactant complexes [4]

The ionic self-assembly strategy is applied to a cationic derivative of the technologically important perylenediimide with its exceptional optical and conducting properties, in conjunction with double tail surfactants of varying length. This yields highly organized thermotropic liquid-crystalline materials.

In order to prove the potential of these novel liquid-crystalline materials for application in devices and as optical components, initial optical investigations were performed. Optical anisotropy was observed by shearing the complexes to a thin film of less than 5  $\mu\text{m}$  thickness onto a clean glass slide. Aligned films of quite good quality were prepared in this way and used to determine the dichroic ratio and to calculate the order parameter. Dichroic ratios higher than 5 and order parameters in the range of 0.6-0.7 were determined.

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Colloids and Interfaces, Golm)

### PAMAM Dendrimer–Fluorosurfactant complexes [5]

Complexes were synthesized making use of amine-functionalised dendrimeric tectons (chemically defined, flexible shape definition) and fluorinated carboxylic acid surfactants. The resulting ordered materials were used as nanoreactors for the preparation of CdS nanoparticles.

### Functional Inorganic Tectons

#### Switchable Cluster-Surfactant Complexes [6]

Facile organization of the inorganic crown-shaped  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anion into room temperature liquid-crystalline materials by complexation with double tail ammonium surfactants via the Ionic Self-Assembly (ISA) route is presented. It is shown by small angle X-ray diffraction, UV-Visible spectroscopy and  $^{31}\text{P}$  NMR analyses that these complexes show an interesting solid-state structure transition. Due to the heating, the inorganic crown species polymerises to the inorganic polyelectrolyte  $^{1\infty}[\text{NiPS}_4]$ . This structural transition is nevertheless reversible, involving a dissolution cycle (Fig. 3).

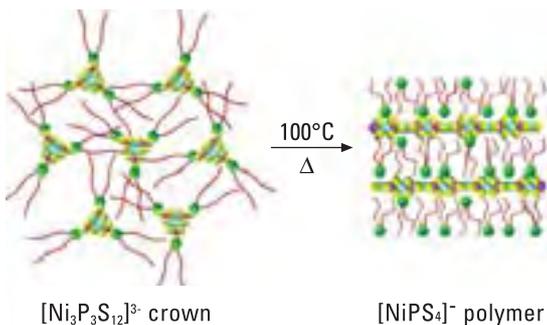


Fig. 3: Inorganic Crown-to-Polymer Switchable System

#### Switchable copper-metallomesogens via ISA: [7]

In a stepwise noncovalent multiple-interaction strategy, copper(II) salts were complexed with the sodium salts of bathophenanthrolinedisulfonic acid ( $\text{C}_{24}$ ) and bathocuproinedisulfonic acid ( $\text{C}_{26}$ ), and organized into nanostructured materials by the addition of ammonium surfactants via the Ionic Self-Assembly (ISA) route. In the case of the methyl-substituted  $\text{C}_{26}$  complexes, a slow color change from green to brick red was observed. UV and EPR investigations showed that the color change was due to a change in oxidation state, yielding brick-red complexes typical for  $\text{Cu}(\text{I})$  species. It is concluded that steric interaction and mechanical packing drive this electronic transition in the metal center into a supramolecular structure (Fig. 4).

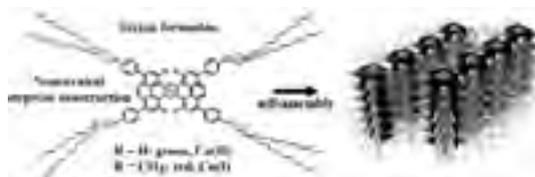


Fig. 4: Multiple interactions for functional nanostructured materials

#### Ongoing Project: Reactions within Confined Molecular Environments (with D. Ganeva): [8]

Polyaddition reactions performed within a highly ordered polyelectrolyte-surfactant monomer complex of polydiallyldimethylammonium chloride and di(undecenyl) phosphate give a 1:1 copy of the original lamellar host structure. No phase disruption or disordering occurs during the reaction. The phase morphology of the host before and after swelling and after polymerization is investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The polymer simplex has improved thermal and mechanical stability.

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# AMPHIPHILIC POLYMERS

## Bioorganic - Synthetic Hybrid Polymers as Molecular LEGO<sup>®</sup> - Bricks



### Abstract

The integration of bioorganic or biomimetic polymers with specific aggregation behavior into synthetic polymer molecules is an approach toward inducing organization in polymeric materials. The structure of the resulting materials and their properties will be analyzed and compared to the ones of unorganized materials. Following this approach "smart materials" with good mechanical properties and responsive to external stimuli are expected.

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Thesis: Applying the Concept of Large Counter Cations to Metal Free Anionic Polymerization of Acrylates and Meth Acrylates

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2000-2001: Postdoctoral Fellow

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Since 2001: Group Leader

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2002: Visiting Researcher

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### Introduction

This project focuses on the development of routes to program structure in polymeric materials. The utilized supramolecular approach is based on the stoichiometric integration of "directing groups" into polymer molecules and the spontaneous or induced self-organization of these groups exploiting molecular recognition mechanisms.

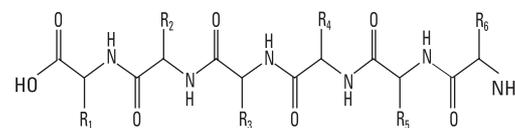
As a result of the organization of the "directing groups", the so-called ordinator\*-groups, structure formation is expected to be induced in the polymer compound on a molecular level.

### Project Description

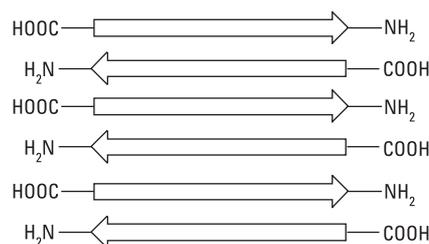
The ordinator-groups will be chosen from the class of bioorganic and biomimetic polymers such as polypeptides, polynucleotides and their artificial derivatives. By using solid phase supported synthesis and successive monomer assemble as polymerization technique, the monomer sequence can be controlled. Thus the ordinator-groups can be achieved in a homodisperse way exhibiting molecular and chemical uniformity.

Due to the defined character of the bioorganic or biomimetic ordinator-groups a multitude of specific aggregation motifs and highly selective aggregation mechanisms can be exploited [e.g. assembling of oligopeptide into anti parallel  $\beta$ -sheet rich quaternary structures (Fig. 1)].

In contrast to the project "Molecular Chimeras" from Dr. H. Schlaad, aggregation behavior is controlled by molecular recognition mechanisms encoded into ordinator-groups by a specific monomer sequence.



a



b

Fig. 1a)  $\beta$ -sheet secondary structure of linear oligopeptide; 1b) anti parallel  $\beta$ -sheet rich quaternary structures.

The synthetic polymer component is expected to be the primary contributor to the mechanical properties of the resulting materials. Therefore, classical synthetic polymers like polystyrene, poly(meth)acrylates, polyamides and polyesters will be utilized. In contrast to the literature where poly(ethylene oxide) [1] is widely used due to its commercial availability or biocompatibility the synthetic polymer should exhibit good mechanical properties.

To realize defined hybrid systems controlled synthesis of the synthetic polymers is required. Furthermore end functionalities like amine, alcohol and carboxylate have to be introduced. Therefore living or "controlled/living" polymerization techniques will be adopted. Depending on the end functionality of the synthetic polymer introduction to the bioorganic compound can be done at complementary functionality either at terminal or at side chain functionalities of the bioorganic oligomer [e.g. oligopeptide (Fig. 2)].

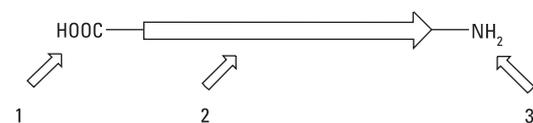
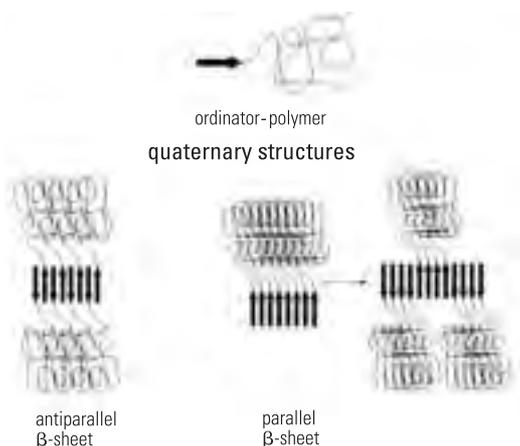


Fig. 2: Introduction of the synthetic polymer, 1, 3) terminal functionalities, 2) Side chain functionality (e.g. Tyrosine, Serine)

\*Ordinator (Latin): guider, disposer, person responsible for arranging the troops in battle formation.

Under proper conditions, the assembly of the ordinator-groups will induce organization of the synthetic polymer. As an example **Fig. 3** shows the aggregation of a hybrid system composed out of an oligopeptide and a synthetic polymer in parallel or anti parallel  $\beta$ -sheet rich quaternary structures.

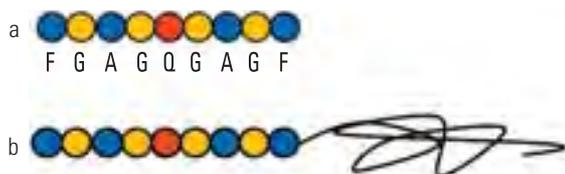


*Fig. 3: Ordinator-polymer hybrid system and targeted aggregation behavior*

During a visit in Stellenbosch University, South Africa in the research group of Dr. Rautenbach (Biochemistry Department) the synthesis of a first model hybrid system via solid phase supported synthesis was investigated.

Inspired by spider silk proteins [2] an amino acid sequence has been extracted. In the native form of the silk protein the function of this segment is to form  $\beta$ -sheet rich quaternary structures. This "crystalline" domains physically cross link amorphous segments to achieve a molecular level structure that is responsible for the excellent mechanical properties of dragline silk high performance fibers.

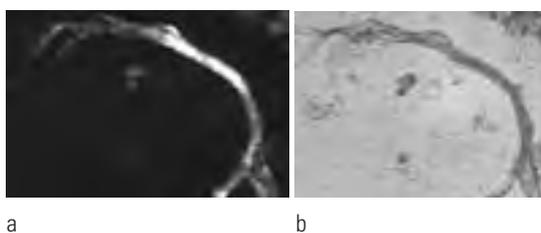
The chosen primary structure (FGAGQ) exhibits a typical polarity sequence (unpolar-nonpolar-unpolar-polar). By artificial extension of this sequence towards a symmetric one (FGAG-Q-GAGF) an oligopeptide with very high tendency to form either parallel or anti parallel  $\beta$ -sheet rich quaternary structures was designed (**Fig. 4a**). The oligopeptide synthesis was done using solid phase supported synthesis following standard Fmoc chemistry protocols. The successful synthesis was confirmed by mass spectrometry (ESI-MS  $M = 811$  D). As synthetic polymer part carboxylate end functionalized polystyrene ( $M_n = 1400$ ,  $M_w/M_n = 1.07$ ) was introduced at the amino terminus of the supported oligopeptide (**Fig. 4b**).



*Fig. 4: Linear hybrid system: a) oligopeptide; b) oligopeptide-polystyrene.*

In preliminary analysis of the aggregation behavior of the oligopeptide the high tendency to form ordered structures like filaments and super structures like fibrils is confirmed (**Fig. 5**). After 3 days at 25°C the pure oligopeptide forms fibril type of supramolecular structures in acetonitrile/water (50/50 v%) which can be observed with light microscopy. The structure exhibits birefringent indicating high molecular order.

Further analysis of the molecular and the supra molecular order of the pure oligopeptide and the hybrid system are in progress.



*Fig. 5: Polarization microscopy micrograph of fibril structures formed by the oligo-peptide: a) polarizer 90°; b) polarizer 0°*

## Outlook

The assembled structured materials should be analyzed in solution and in bulk. Potentially functional materials can be achieved having the probability to response to an external stimuli e.g. change in pH-value, temperature, ionic strength or light irradiation. These responsive materials will have applications in areas of tissue repair, bioadhesive or -compatible materials or pH-sensitive drug release systems.

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## Biomimetic Mineralization



We have continued our efforts to explore the potential of biomimetic mineralization processes using simple model polymers for proteins which are active in biomineralization processes, the so called Double Hydrophilic Block Copolymers (DHBC's) [1]. These polymers consist of two water soluble blocks where one block can interact with a crystal surface and the other one just provides water solubility [e.g. Poly(ethylene oxide)] so that these polymers serve as a tool to provide nm sized building blocks for further self assembly into complex structures. We were successful in expanding our set of block copolymers to functional poly(ethylene imine) blocks modified by carboxylate, sulfonate, phosphonate and thiol groups as well as hydrophobic moieties [2], monophosphate ester [3], polyoxazoline [4], and various polypeptide blocks [5]. Polypeptides are sometimes already itself active in crystal morphogenesis in a limited experimental range [6]. These DHBC's could serve numerous purposes. In the simplest case, they could be used for nanoparticle stabilization in water. For the stabilization of high quality CdS using poly(ethylene imine) block copolymers with different architectures of the PEI block, it could be shown that branched functional blocks have the highest activity compared to linear or dendritic blocks [7]. In addition, the nanoparticle size could be simply controlled by the block copolymer concentration and the electron donating functional amine groups protected the semiconductor against photocorrosion. This indicates that tailor made DHBC's can fulfill multiple tasks.

Such stabilized nanoparticles can be used for the self-assembly of complex structures, if the stabilizing PEO block is short enough to allow only for a temporary stabilization. If  $\text{CaCO}_3$  nanoparticles are temporarily stabilized by DHBC's with monophosphate functional moieties, and the crystallization is carried out via a  $\text{CO}_2$  evaporation technique,  $\text{CaCO}_3$  is formed at the air water interface and emerging  $\text{CO}_2$  gas bubbles can be used as a template for complex  $\text{CaCO}_3$  structures according to Fig. 1 [4]. Here, the water surface tension determines how big the aggregate structures can grow before they sink to the bottom. This shows that already a very simple template like a gas bubble can be used for the production of complex morphologies and indicates the potential of using DHBC stabilized nanoparticles for hierarchical self-assembly.

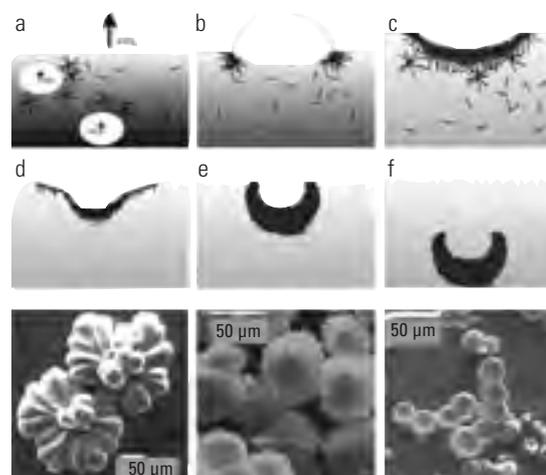


Fig. 1: Upper scheme: Aggregation mechanism of temporarily DHBC stabilized  $\text{CaCO}_3$  nanoparticles with a  $\text{CO}_2$  gas bubble as template. The lower figures represent the obtained structures with from left to right decreasing water surface tension.

However, it is also possible to form complex higher order assemblies without templates. This was demonstrated for  $\text{CaCO}_3$ , and it could be shown that beside the choice of the block copolymer, experimental parameters like the pH or the  $\text{CaCO}_3$ /polymer concentration ratio are also important for the morphogenesis [8]. It is remarkable that a rod-dumbbell sphere transition was observed in a kinetic study, which was speculatively explained by the action of intrinsic electric fields [9] and that the initially observed nanoparticles are amorphous. If a slow gas diffusion precipitation technique is used under otherwise unchanged conditions, these particles grow to a much bigger size of up to  $100 \mu\text{m}$  and are finally overgrown by calcite rhomboeders which make them a promising chromatography column filling material due to the exposition of multiple calcite faces [10].

Another interesting morphogenesis scenario, also starting from amorphous precursor aggregates was observed for  $\text{BaSO}_4$  in presence of a partially phosphonated poly(ethylene oxide)-block-poly(methacrylic acid) block copolymer, which resulted in the formation of fiber bundles consisting of defect free single crystalline fiber bundles [11]. The mechanism as outlined in Fig. 2 was also speculatively explained with the action of intrinsic electric fields, although a literature reported oriented attachment mechanism for the removal of high energy surfaces could explain the results equally well.

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### References

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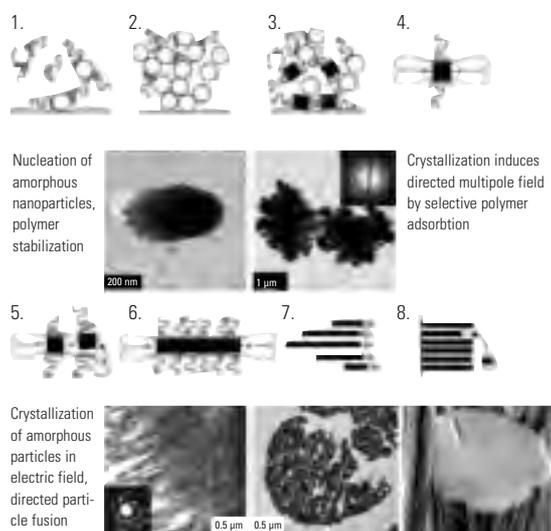


Fig. 2: Mechanism of the polymer mediated formation of single crystalline  $\text{BaSO}_4$  fibers [11]

Similar results were obtained with the structurally identical  $\text{BaCrO}_4$  and the role of various block copolymer functional patterns as well as experimental conditions was explored in detail [12]. DHBC's can also modify crystal morphologies by face selective adsorption. An example is the forbidden 10-fold symmetry of a single flower-like  $\text{BaSO}_4$  crystal, which could be obtained by face-selective polymer adsorption and the resulting modification of the growth [13]. The formation of this unusual morphology could be explained by a multi-step growth mechanism and shows that the polymer influences the crystal growth on different hierarchies.

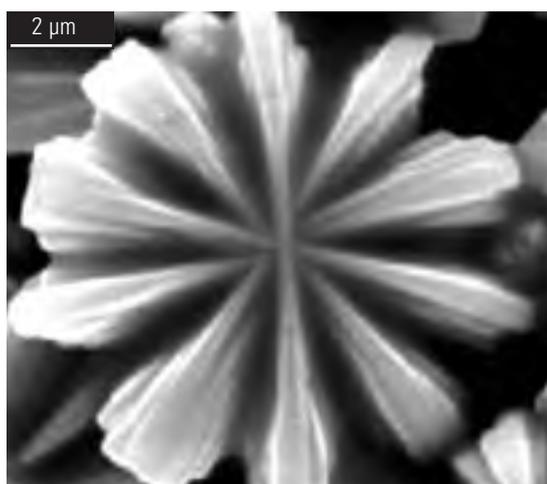


Fig. 3: Single-crystalline  $\text{BaSO}_4$  flower-like morphology obtained in the presence of a sulfonated Poly(ethylene oxide)-block-poly(ethylene imine) DHBC [13]

In addition to these fundamental studies, we explored the DHBC modified crystallization also for functional materials. For  $\text{CdWO}_4$ , we were able to synthesize very thin nanoparticles, which showed an improved fluorescence behavior compared to the default material. This was attributed to the modified crystal morphology with perfect crystal structure as well as to a quenching of surface defects [14].

Beside the crystallization modification of inorganic materials, DHBC's were also found to be active with other materials. It could be shown that the structure of liquid water and ice can be modified by poly(ethylene oxide)-block-poly(hydroxyethyl ethylene) and its partially phosphorylated derivative, resulting even in changes/distortions of the ice unit cell [15]. This indicates that the role of DHBC's as additives for crystallization control may be more complicated than so far assumed, as all crystallizations are performed in water. When chiral functions are added to a DHBC, it appears possible that the fundamentally and industrially important separation of a racemic mixture into the enantiomers can be achieved by selective DHBC interaction with one enantiomer upon crystallization. We were able to show that beside the morphology modification of calcium tartrate tetrahydrate, an enantiomeric excess of about 40 % could be achieved, when the racemic mixture was crystallized in presence of a chiral DHBC, although the racemic crystal is thermodynamically stable [16]. With time, the enantiomeric excess decreased due to reformation of the racemic crystal indicating that a successful racemate separation by crystallization modification can only be achieved by kinetic control.

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## Amphiphilic Block Copolymers



The research of the work group is devoted to the following topics: (i) development of new controlled polymerization techniques, (ii) characterization of polymers with fractionation methods, and (iii) study of the phase behavior of amphiphilic diblock copolymers.

Regarding the latter, it is the main focus to examine the effects of  $\beta$ -structures and specific interactions on structure formation on the nanometer length scale. It is expected (or rather known) that additional contributions to the mixing free energy lead to other, more complex superstructures than the classical BCC, HEX, or LAM. The systems we are particularly interested in are "molecular chimeras" of synthetic polymers and  $\alpha$ -helical polypeptides, diblock copolymers with metal-binding sites, and polyion complexes of oppositely charged block ionomers.

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Thesis: Studies of the mechanism of the anionic polymerization of methacrylates in the presence of aluminium alkyls in toluene.

**1998:** Postdoc (University of Massachusetts, Lowell, USA)

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

### Publications:

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**[2]** Schlaad, H., Kukula, H., Rudloff, J., Below, I.: Synthesis of  $\alpha$ ,  $\omega$ -hetero-bifunctional poly(ethylene glycol)s by metal-free anionic ring-opening polymerization. *Macromolecules* 34, 4302-4304 (2001).

**[3]** Schlaad, H., Kitz, P.: Determination of molecular weight distributions of diblock copolymers with conventional size exclusion chromatography. *Anal. Chem.* 75, 1548-1551 (2003).

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### "Molecular Chimeras" of Synthetic Polymers and Polypeptides

Linear and star-shaped block copolymers were synthesized via the ring-opening polymerization of  $\alpha$ -amino acid N-carboxyanhydrides ( $N^{\epsilon}$ -Z-L-lysine and  $\gamma$ -benzyl-L-glutamic acid) initiated by  $\omega$ -amino-functional polymers (polystyrene, polybutadiene, **[1]** and poly(ethylene glycol) **[2]**). Block copolymers were analyzed by means of NMR, size exclusion chromatography, and analytical ultracentrifugation. Samples usually exhibit a monomodal distribution with a polydispersity index in the range of 1.2-1.8 **[3, 4]**. However, branched samples could not yet be analyzed with respect to number and distribution of polypeptide grafts.

Linear polystyrene-block-poly(Z-L-lysine)s adopt a hexagonal-in-lamellar structure in the solid state, irrespective of composition. Analysis of structural details revealed that the interfaces between layers are not planar but undulated. Samples with a star-shaped architecture also arrange in lamellar structures, but the intersheet distance is always  $\sim 20$  nm. It is evident that polypeptide brushes stabilize a larger surface area than linear chains, thus enhancing the generation of undulations. Depending on the conformation of the polypeptide chains, either planar, superundulated, or corrugated lamellar phases can be formed (see the generalized phase diagram in **Fig. 1**,  $\iota$  = averaged normalized interface area;  $\kappa$  = normalized scattering-average of curvature).

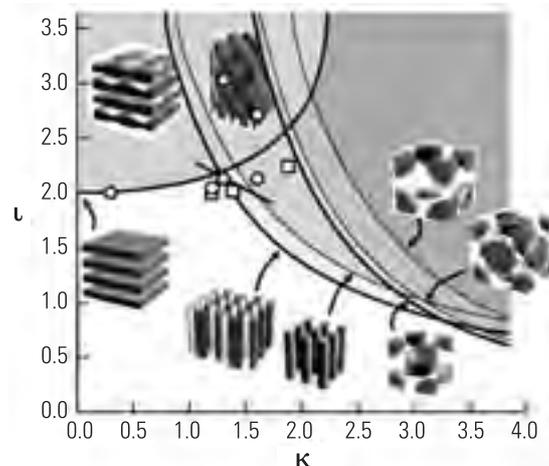


Fig. 1

In dilute aqueous solution, polybutadiene-block-poly(L-glutamate)s can aggregate into spherical micelles or large vesicles/"peptosomes" ( $R_h \sim 70$  nm), depending on the chemical composition of the copolymer. The polypeptide corona can undergo a pH-induced coil-helix transition without seriously altering the size and morphology of aggregates (**Fig. 2**) **[6]**.

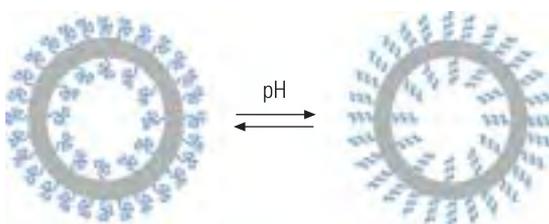


Fig. 2

Linear and star-shaped polystyrene-block-poly(D,L-glutamate)s were used in emulsion polymerization to produce electrosterically stabilized polystyrene latexes with a polypeptide corona **[7]**. The main latex properties, namely the average particle size, distribution, electrolyte stability, and electrophoretic mobility, were strongly affected by the architecture of the stabilizer. Star-shaped stabilizers exhibit a higher stabilizing efficiency than linear ones and are able to stabilize a second generation of particles, producing bimodal dispersions.

### Diblock Copolymers with Metal-Binding Sites

Well-defined block copolymers with  $\beta$ -dicarbonyl chelating segments (**Fig. 3**) were synthesized (for the first time) via two different routes: (i) synthesis of copolymers with a poly-alcohol segment by living anionic or group transfer polymerization and subsequent azeotropic acetoacetylation of hydroxyl units **[8]** and (ii) reversible addition-fragmentation chain transfer (RAFT) radical polymerization of 2-(acetoacetoxy)ethyl methacrylate **[9]**. The obtained polymers usually exhibit monomodal and narrow molecular weight distributions (polydispersity index < 1.2).

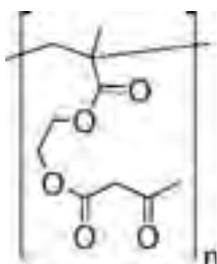


Fig. 3

In cyclohexane, poly(*n*-butyl methacrylate)-block-poly(2-(acetoacetoxy)ethyl methacrylate)s form spherical or cylindrical micelles ( $R_h=10\text{-}50\text{ nm}$ ). Aggregation numbers were found to be much higher than what is reported for other micellar systems. The higher density of chains at the core-corona interface is presumably due to attractive interactions between acetoacetoxy units via hydrogen bonding **[10]**.

These micellar aggregates were used to solubilize various metal ion salts in media, in which otherwise they were totally insoluble (e.g.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in cyclohexane). Poly( $\beta$ -dicarbonyl) block copolymers were also used as additives for biomimetic mineralization processes and for the nano-casting of inorganic materials.

### Polyion Complexes of Block Ionomers

By mixing dilute solutions of oppositely charged block ionomers with strongly segregating solvating segments ( $\chi_{\text{N}} \sim 40$ ), namely polybutadiene-block-poly(cesium methacrylate) and polystyrene-block-poly(1-methyl-4-vinyl-pyridinium iodide), polyion complexes are formed which self-assemble into vesicular aggregates ( $R_h \sim 65\text{ nm}$ ). These vesicles exhibit a phase-separated microstructure (**Fig. 4**) and are thus amphiphilic in nature. Which of the segments is forming the outer and inner layer of the vesicle membrane can be controlled by the selectivity of the solvent, i.e., these vesicles are able to respond to an external stimulus **[11]**.

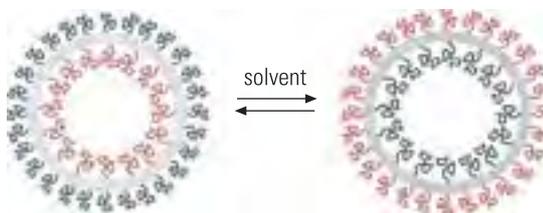


Fig. 4

This modular approach shall be used to generate a library of complex superstructures with reduced or even broken symmetry ("Janus micelles").

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## Porous Materials via Nanocasting Procedures: Innovative Materials and Learning about Softmatter Organization



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Nanocasting, the 3D-transformation of self-assembled organic nanostructures into hollow inorganic replicas under preservation of fine structural details has recently turned out to be a versatile tool in colloidal material science. In nanocasting or the “true lyotropic liquid crystal approach”, as introduced by Attard and Göltner, one starts from a high concentration ordered template phase, and the liquid continuous phase is just solidified by chemical gelation reactions [1]. Already in previous work, it was shown that this technique offers the possibility to make a 1:1 imprint or negative copy of the organic mesophases. X-ray measurements performed throughout the process showed that the solidified hybrid preserves all structural features throughout solidification of the matrix, and even the calcined or hollowed replica possesses the same structure, and only slightly shrinks. To enable nanocasting, the casted structure must be compatible with both the liquid precursor phase as well as the final solidified replica. If this is not the case, the enormous interfaces involved (up to 1000 m<sup>2</sup>/g) will add unfavorable energies, and replication breaks down.

In the report period, we have tried to learn about the mechanistic aspects of this procedure. Major work was attributed to the quantitative SAXS and SANS characterization of those samples [6, 14, 15].

It was shown that a so-called “three-phase” model described the whereabouts of the template in the matrix, and that micropores are an inevitable side-product on the concept, as solvating moieties stay mixed with the silica phase.

Beside diverse amphiphilic block copolymers (Fig. 1), the base of possible templates was significantly extended. Mixtures of different non-ionic surfactants allowed the adjustment of pore size with Angstrom precision and also gave a cohesive picture about the general process of mixed micelles formation [9].

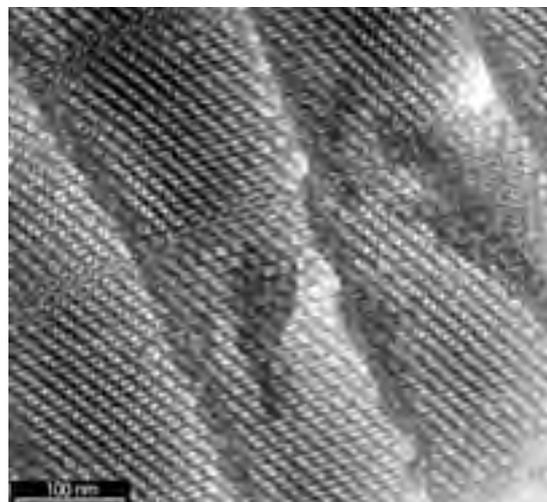


Fig. 1: Porous silica made by nanocasting of the FCC micellar phase of an amphiphilic block copolymers

Fig. 2 depicts the experimental and fitted dependence of pore radius on both the hydrophilic and hydrophobic length of the surfactants, as established by about 20 different samples.

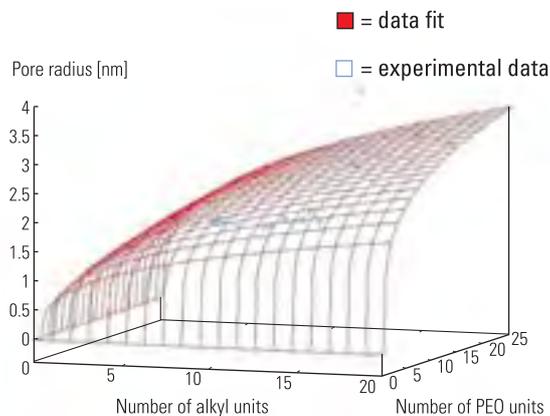


Fig. 2: Angstrom-control of worm-like pores by appropriate choice of commercial surfactants and their mixtures

Cyclodextrines (CDs) as templates not only allowed to depict the natural self-organization of CDs [7] and their supramolecular complexes with polymers, the pseudorotaxanes [2], they also were the base for a simple one-step synthesis of nanoparticle@porous silica systems [8], promising candidates for the rational synthesis of heterogeneous catalysts. In another set of experiments, the same system was used as a conceptual new solar energy absorber, where efficient IR-emission was spectroscopically excluded [5].

Another case where the analytical potential of nanocasting was favourably used is found in the characterization of the interaction of polyelectrolyte thickeners with surfactant formulations [3], an admittedly industrial driven question.

The actual work on new templates is exploring the potential of new systems, such as room temperature ionic liquids (RTILs), which have the potential advantage to work also in the absence of water, thus allowing a much broader chemistry for the generation of the porous host.

First work in this direction where the RTIL is used as solvent and template simultaneously indicates the extraordinary potential of this class of substances, such as the generation of crystalline lamellar materials (Fig. 3).

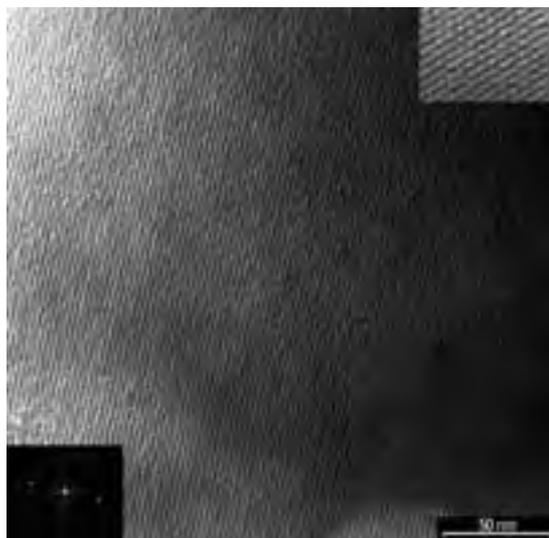


Fig. 3: Nanostructured hybrid material with a lamellar structure with 2.7 nm repeat period. Inlet 1: electron diffraction; inlet 2: magnification of the structure

Other current work is dealing with chiral templates and corresponding chiral pore systems, such as cellulose derivatives or ionic surfactant assemblies with chiral counterions. A chiral pore system would have the advantage to overlay chiral properties in an otherwise non-chiral system, e.g. by filling dye solutions into the chiral silica. In addition, we can examine the question of chiral recognition in chromatography, i.e. is it just the imprinted molecule which is bound or is there a general chiral polarization force.

The broad accessible variety of pore sizes and surface structures is also used to exert control of chemistry through confinement in space ("nano-chemistry"). In cooperation with the University of Potsdam, the altered thermodynamics of excimer formation in confined space is examined. Together with colleagues from Marburg, we examine the possibility to make new objects out of engineering plastics and carbon, using the diverse well-defined pores again as moulds for reaction.

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## Templating Strategies to Fabricate Controlled Morphology Networks



Nanocoating, the covering of materials with a layer on the nanometer scale, or covering of a nanoscale entity, using the sol-gel process is a powerful tool for the preparation of nanocomposites and structured materials [1]. Spherical nanoparticles, porous membranes [2], polymer fibers [3] and gels [4], or porous polymeric beads [5] can be used as templates. A combination of porous membrane templates

with amphiphilic supramolecular aggregates makes possible the synthesis of materials with bimodal pore structure [6]. The inorganic framework usually consists of metal oxides which have numerous applications in catalysis and photovoltaics. The main research goal is the production of novel inorganic networks that have high surface areas as well as high porosity. These properties increase the number of accessible catalytically active sites and provide enhanced flow rates.

### Titanium Dioxide Tubes:

A sol-gel procedure has been applied for the metal oxide coating of polymer fibers. For coating, the poly(L-lactide) fibers were soaked in a titanium alkoxide precursor solution and subsequently hydrolysed in a water/isopropanol mixture. Thermal treatment at 500 °C removed the polymer leaving a hollow titanium dioxide structure of interwoven fibers [3]. Fig. 1a shows an SEM image of the final titanium dioxide tubes. The diameter of the inorganic material is dependent on the initial polymer fiber, with some shrinkage occurring during the heating process. The tube wall thickness is below 200 nm. According to TEM images indentations in the poly(L-lactide) fibers are filled with the metal oxide leading to secondary structures within the tubes (Fig. 1b).



Fig. 1a: SEM image of the hollow titania fibers, b: TEM image of the tubes showing the mimicking nature of the sol-gel coating technique (scale bar is 5  $\mu\text{m}$ )

### Porous Silica and Titania Spheres:

The sphere with its simple morphology allows for improved flow properties and is ideal for adsorption or chromatographic packing. Spherical beads that are porous throughout can be used to improve the properties of a material, due to increased accessible surface plus the added benefits of smaller pore characteristics. The use of polymeric beads as templates has been examined for the formation of silica and titania spheres with porous inner structuring [5]. This approach allows direct control of the final sphere size, which is dependent on the initial bead diameter. The porous organic beads were composed of polystyrene cross-linked with divinyl benzene. Both titania and silica spheres were obtained by applying the sol-gel, where the alkoxide precursor underwent hydrolysis and condensation reactions to form the metal oxide within the organic structure. On calcination of the hybrid spheres, the organic material is removed, leaving the inorganic, porous spheres. Fig. 2a shows the titania spheres. They are monodisperse, and the porous surface structure is visible.

The TEM image in Fig. 2b shows that the inner structure of the titania spheres is porous and that the spheres consist of nanoparticles with diameters between 20 and 70 nm. The surface area of the porous inorganic spheres varies substantially for the titania and silica spheres. The crystalline titania exhibits BET specific surface areas in the range of 30 to 35  $\text{m}^2/\text{g}$ , whereas the amorphous silica has surface areas between 550 and 700  $\text{m}^2/\text{g}$ .

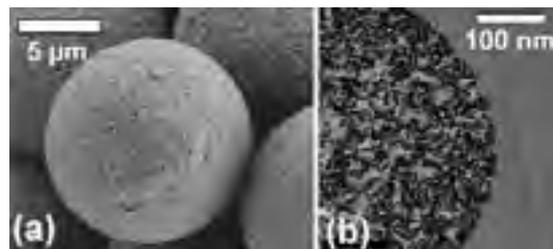


Fig. 2a: SEM image of titania spheres, b: TEM cross-section of a titania sphere consisting of individual nanoparticles

### Macroporous Titania and Titania/Zirconia:

A variety of polymer gels with different chemical composition, architecture, porosity, and surface area have been used as templating materials for the fabrication of porous titania and titania/zirconia networks [4, 7]. The homogeneously porous polymer gel with a globular structure (Fig. 3a) is placed into alkoxide solutions of the corresponding metal(s). After hydrolysis and condensation the metal oxide/polymer hybrid was heated to 500 °C to remove the organic template and to induce crystallization of the amorphous inorganic gel. An SEM image of the resulting titania material is shown in Fig. 3b. The structures prove that a coating of the initial polymer was obtained, yielding a hollow globular material on removal of the template.

An overall shrinkage of about 20 % can be observed when comparing the initial gel and the final inorganic structures. The samples produced using a mixture of titanium and zirconium alkoxides gave similar SEM images.

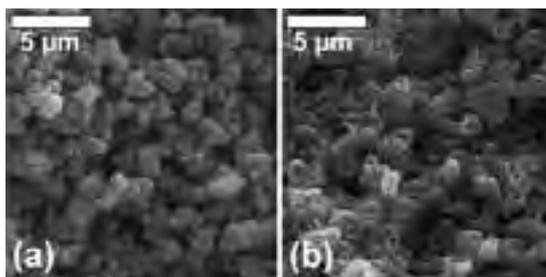


Fig. 3a: SEM image of the initial polymer gel template, b: SEM image of the final titania network

According to X-ray analysis the titania samples mainly consist of anatase nanocrystals with traces of the rutile modification. The addition of 10 mol% zirconia stabilizes the anatase form, whereas a further increase of the zirconia content inhibits crystallization. Samples containing zirconia as the major component can be assigned to either the monoclinic or tetragonal modification of zirconia.

The surface areas vary from 30 to 40 m<sup>2</sup>/g for titania and from 26 to 126 m<sup>2</sup>/g for the mixed titania/zirconia networks. The crystalline systems have lower surface areas than the amorphous ones.

### Bimodal Silica Films:

Using simultaneously tetramethyl orthosilicate as silica precursor, porous membrane templates and amphiphilic supramolecular aggregates as porogens, extended porous silica films with thicknesses in the range of 60 to 130 µm and pores on both the meso- and macro-scale have been prepared [6]. The macropore size is determined by the cellulose acetate or polyamide membrane structure and the mesopores by the chosen block copolymer or non-ionic surfactants. Both the template and the porogen are removed during an annealing step leaving the amorphous silica material with a porous structure which results from sol-gel chemistry occurring in the aqueous domains of the amphiphilic liquid-crystalline phases and casting of the initial template membrane. SEM (Fig. 4a) and TEM images (Fig. 4b) show the macro- and mesoporous morphology of the silica materials, respectively. The surface area and total pore volume of the inorganic films vary from 470 to 850 m<sup>2</sup>/g, and 0.50 to 0.73 cm<sup>3</sup>/g, respectively, depending on the choice of template and porogen.

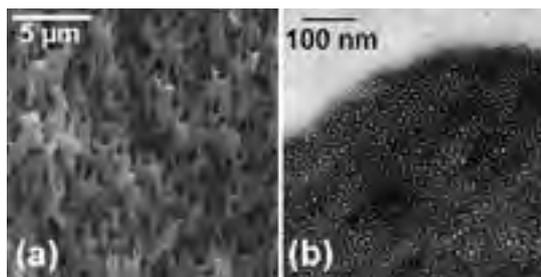


Fig. 4. a) SEM and b) TEM images of the silica material giving evidence for the bimodal porous structure.

### Photocatalytic Properties of Porous Metal Oxides:

Investigations of the photocatalytic activities of different porous materials such as titania, titania/zirconia, and titania/indium oxide obtained from a polymer gel templating technique have been performed in comparison with Degussa P25 [7, 8]. In the photodecomposition of salicylic acid and 2-chlorophenol, the titania-containing structures showed excellent photocatalytic activity, with efficiencies better than the Degussa P25 standard. The presence of the second metal oxide in the titania structure even leads to an increase in photocatalytic activity.

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## Fractionating Colloid Analysis



This project is focused on the analysis of complex mixtures by fractionating techniques namely Analytical Ultracentrifugation (AUC) and Field-Flow-Fractionation (FFF). The main advantage of these techniques is that they operate without stationary phases so that an undesired sample-column interaction can be excluded. In the past, our AUC work was focused on the determination of particle size distributions of

smallest nanoparticles down to sizes even below 1 nm. These efforts are continued both, on the service basis for the institute as well as on a research basis [1] with the goal of the latter to explore the possibilities for the determination of critical crystal nuclei or subcritical complexes in solution to allow conclusions about particle growth mechanisms. An example for the high resolution of such particle size distributions is given in Fig. 1 for  $ZrO_2$  which was quenched during particle growth.

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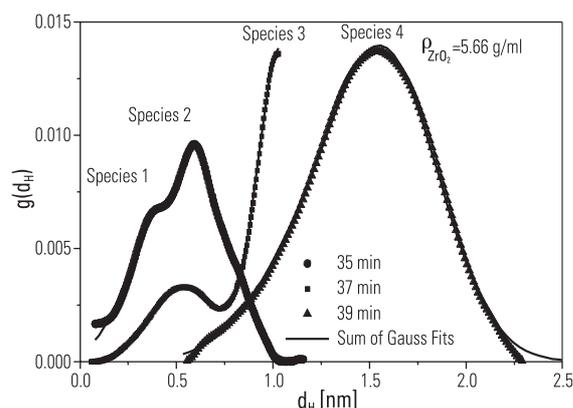


Fig. 1: Apparent particle size distributions of growing  $ZrO_2$  prepared by acid hydrolysis of  $Zr(SO_4)_2 \cdot 4 H_2O$  at  $70^\circ C$  and quenched in liquid  $N_2$  after different reaction times [2]

It can be clearly seen that the small species are subcritical complexes with Angström size. However, a serious drawback is that the determined particle size distributions depend on the density of the particles which is unknown in most cases for very small species at the transition from molecules to solid bodies. The workaround of determining the particle size distributions for two extremes of densities to give a particle size range is not satisfying. A further problem exists for the assignment of the detected species as their size is only given as a hydrodynamic equivalent diameter. Therefore, we tried to develop an equilibrium method for the detection and preparative isolation of critical crystal nuclei. To achieve this, a dynamic equilibrium between crystallization and dissolution of a crystal has to be established which is potentially possible using a pH gradient in the ultracentrifuge cell according to Fig. 2.

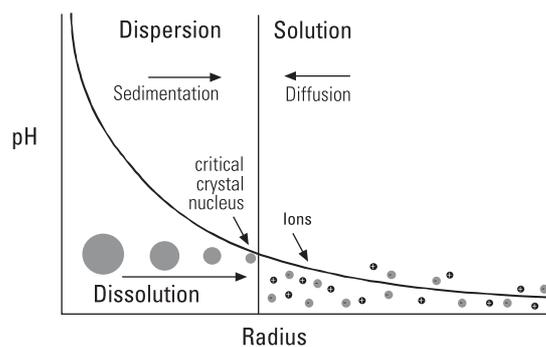


Fig. 2: Dissolution of a crystal in a pH gradient [3].

Here, a crystal can gradually dissolve upon sedimentation as the pH is steadily decreasing towards the bottom of the centrifuge cell. At a certain position, the crystal will dissolve completely into ions which have a higher diffusion coefficient and thus diffuse back into regions of higher pH which should lead to a supersaturation and thus crystallization, so that it should be possible to generate a narrow band where crystallization and dissolution are in a dynamic equilibrium which is the critical crystal nucleus per definition. Although it was possible to generate such pH gradients by sedimentation of a polyacid and equilibrium conditions could be proven, it was not yet possible to isolate critical crystal nuclei, although some indications for their presence were found by AUC [3]. Solubility gradients in the ultracentrifuge can also be generated using ionic strength gradients or via solvent mixtures and their potential is under exploration for the isolation of critical crystal nuclei as well as for other applications which can take advantage of a continuous gradient of a physicochemical property like complex dissociation, protein unfolding, electron gradients etc.

Chemically reacting or organic-inorganic hybrid systems are important but notoriously difficult systems for the characterization of their particle size distribution. In that respect, we could show for the synthesis of iron oxide nanoparticles inside lumazine synthase capsids, that already sedimentation coefficient distributions can yield remarkable insight into the system reflecting structural or compositional changes of the sample [4]. Also, chemically reacting systems can be characterized with high statistical accuracy if it is possible to completely quench the chemical reaction. This was shown for nanoparticle-enhanced turbidimetric immunoassays where an antibody coated latex mixture with different sizes and antibody reactivities reacted with the antigen CRP [5]. The mixture was designed in a way that at low antigen concentrations, only the bigger latices aggregate whereas at higher antigen concentrations, the smaller latices aggregate as well and this mechanism could be proven (Fig. 3).

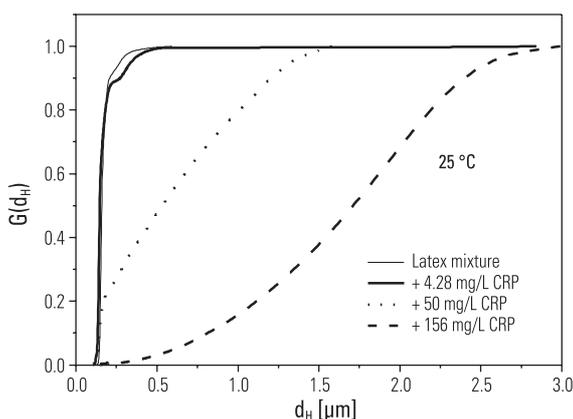


Fig. 3: Mass weighted integral AUC particle size distributions of an agglutinated latex mixture at different CRP concentrations after 10 min at 25 °C. [ $d_H$  = Diameter of the particles,  $G(d_H)$  = Integral particle size distribution].

Beside the important application of AUC for particle size analysis, the technique was also applied for the more classical solution analysis of macromolecules, both as service for the institute and as research. Here, especially chitosans were of interest due to their biocompatibility and polycationic properties. In combination with light scattering, the hydrodynamic solution structure could be determined beside molar mass and other standard parameters [6, 7] and it could be shown that chitosan is not as extended, as it was described in the previous literature indicating the potential of combining AUC with other techniques like light scattering. Such combination is currently also investigated for AUC & FFF coupling which shows special promise for the analysis of complex hybrid colloid mixtures. Beside the soluble systems, biopolymer gels were also investigated with respect to their demixing in an ultracentrifugal field [8].

Although AUC has proven its versatility and fractionation power for many colloidal systems a present limitation are the optical detection systems which can only detect light absorbance or refractive index changes. In addition, the adsorption optics is slow and of bad quality. We therefore started a joint project with a partner from chemical industry concerning the development of improved or new detectors for AUC. We have started the development of a fiber optics based UV-Vis detector which is able to acquire a whole spectrum in as little as 2ms and have currently finished the hardware set-up. Such spectrometer should even allow the observation of chemically reacting systems in the future.

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## Electron Microscopic Studies of Colloidal Systems



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**1977:** Diploma, Physics (Humboldt-Universität zu Berlin; Institute of Low-Temperature Solid State Physics)

Thesis: Application of square-wave polarography and a density method for the analysis of bismuth-antimony alloys

**1977–1991:** Research Scientist (Institute for Polymer Chemistry, Teltow)

**1987:** PhD, Polymer Physics (Institute of Polymer Chemistry, Teltow)

Thesis: Contribution to the formation mechanism of coagulation structures of polymers using electron microscopy

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The chemical and physical properties of colloidal nanostructured materials depend sensitively on their chemical composition, the size of the structural elements and their spatial arrangement in the system and the media in which the components are dispersed. The dimensions of dispersed particles, pores or the mesh size of polymer networks, are in the range of 1 nm to 1  $\mu\text{m}$ . Transmission and scanning electron microscopy have proved to be powerful analytical methods to investigate the relationship between the synthesis conditions and morphological structure. So, we are working closely together a number of groups of the colloid chemistry and interface departments.

In the last two years, we have focused our research activities on the investigation of the morphological structure of polymer micelles, inorganic crystals, metal colloids, microporous silica and polymer particles produced by heterophase polymerization techniques.

These studies are important to analyze, e.g., the complex structure formation processes in miniemulsions in the presence of colloidal silica particles. Under alkaline conditions well-covered polymer particles can be formed (**Fig. 1**). A mixture of styrene and 4-vinylpyridine is used as the monomers. The diameter and morphology of latex particles can be varied as functions of the composition of the system, the pH, and the adsorption of cationic components.

There is a continued scientific interest in the formation of inorganic solids with well-defined properties such as size, shape, and surface roughness. Calcium carbonate ( $\text{CaCO}_3$ ) has been used as a model system for studying the biomimetic synthesis of  $\text{CaCO}_3$  crystals in the presence of organic templates and/or additives.

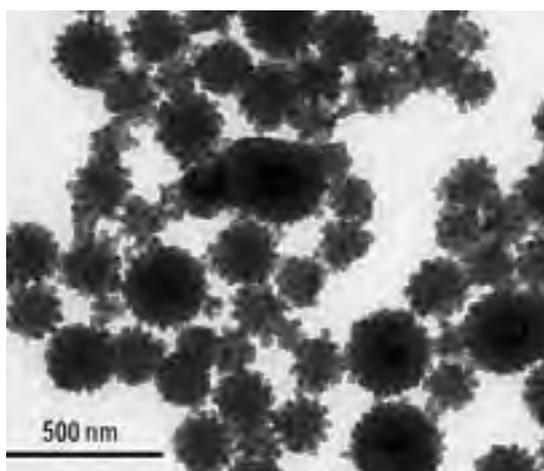


Fig. 1: Latex particles with a monomer to silica ratio of 1:0.64

To modify the morphology of the crystals, special double-hydrophilic block copolymers are used.

The biomimetic crystallization of  $\text{CaCO}_3$  was realized by a slow gas-liquid diffusion reaction of  $\text{CO}_2$  in the presence of poly(ethylene glycol)-block-poly(ethyleneimine)-poly(acetic acid) (PEG-b-PEIPA). The slow precipitation process leads to the formation of uniform spherical crystals. After few days the system contains a variety of intermediates (**Fig. 2**) with different shapes such as elongated rods (a), peanuts (b), dumbbells (c), and overgrown spherical particles (d). After two weeks of ripening, and on reaching equilibrium, all particles have a spherical superstructure with a nearly uniform diameter of around 80  $\mu\text{m}$ . Their surface is composed of smaller truncated and randomly oriented calcite crystallites with an average size of about 2-5  $\mu\text{m}$ . The biomimetic crystallization of  $\text{BaCrO}_4$  and  $\text{BaSO}_4$  in the presence of sodium polyacrylate yields highly-ordered funnel-like  $\text{BaCrO}_4$  superstructures with a complex form and a remarkable self-similar growth pattern as well as long  $\text{BaSO}_4$  fibre bundles (**Fig. 3**). The crystallization can be affected by variation of temperature, pH, and concentration.

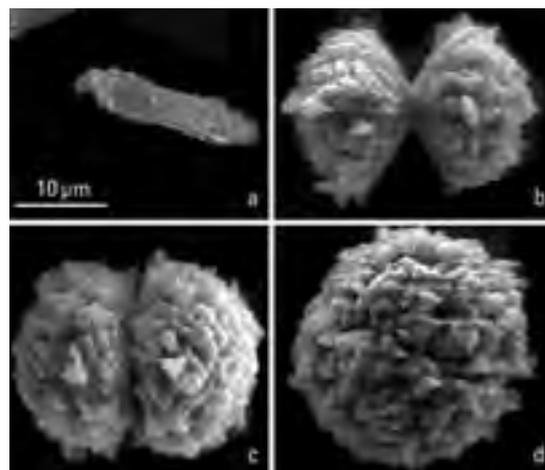


Fig. 2: Different  $\text{CaCO}_3$  crystals showing the morphological evolution process

In the field of crystal engineering, there are special strategies which allow one to control the parameters of the crystallization process. Some of these concepts use restricted reaction environments. The morphology of a range of inorganic crystals, growing inside micrometer-sized polyelectrolyte-complex capsules was studied. The diameter of the selectively permeable capsule walls depends on the size of the templates and can be varied in the range of 0.2  $\mu\text{m}$  to 10  $\mu\text{m}$ .

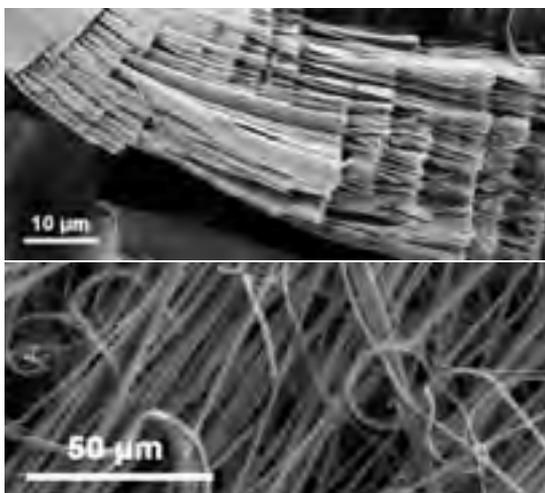


Fig. 3: Highly-ordered funnel-like superstructure (top) and nanofibers of  $\text{BaSO}_4$

In Fig. 4a are shown  $\text{BaCO}_3$  crystals which are grown within the polyelectrolyte capsules. With additional energy-dispersive X-ray analysis (EDS) we have determined the chemical composition of the inorganic nanoparticles (Fig. 4). The gold peaks result from the soft gold sputtering process used to avoid charge effects during the measurement.

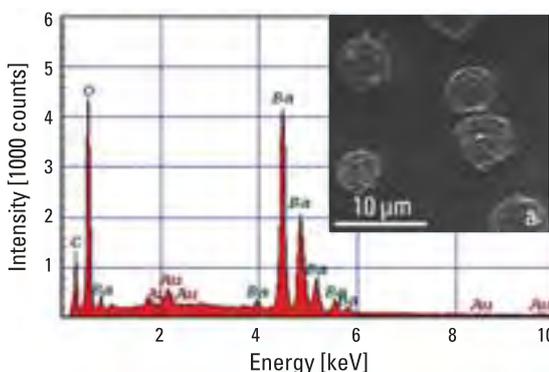


Fig. 4:  $\text{BaCO}_3$  nanoparticles within polymer shells (a) and the characteristic EDS spectrum

Another interesting field in colloid science we are studying is the formation of polymer capsules containing metal colloids that are useful for catalytic applications. To characterize, e.g., silver colloids inside the polymer shell, we studied the morphology of the empty capsules with TEM. The structure of the shells containing silver nanoparticles can be varied. Two systems of polymer shells containing different nanosized silver particles are shown in Fig. 5a and Fig. 5b.

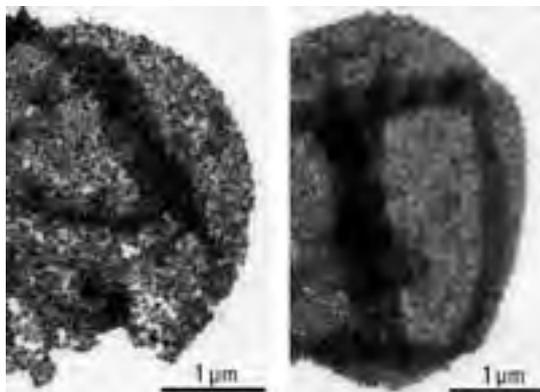


Fig. 5: Empty PSS-Ag capsules. Reduction before dissolution of the core (left) and after that (right)

In cooperation with the Department of Physical Chemistry of the University of Hamburg, interesting phase morphologies of poly(butadiene-*b*-ethylene oxide) (PB-PEO) block copolymer hydrogels are studied using critical-point drying and cryo-ultramicrotomy. In Fig. 6 the structure of a self-assembled PB-PEO block copolymer hydrogel at a polymer weight fraction of 0.8 is shown. The lamellar spacing depends on the molecular parameters and the composition of the polymer/water mixtures, and can be precisely depicted using transmission electron microscopy.

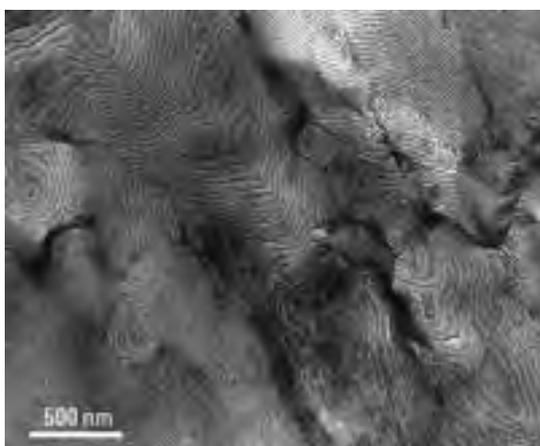


Fig. 6: Lamellar structure of PB-PEO block copolymer hydrogel

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## Gel Permeation Chromatography (GPC), Static Light Scattering (SLS)



### GPC:

We focus on methods and equipment allowing simultaneous RI (refraction index), UV (ultraviolet spectrophotometric) and MALLS (multi-angle laser light scattering) detection. The research is influenced by actual characterization problems in cooperation with projects from the colloid chemistry and interfaces departments of the institute.

### Gudrun Rother

1963: Diploma, Physics

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Thesis: Relativistische Theorie der Mechanik der Kontinua

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Thesis: Untersuchung der Wechselbeziehungen zwischen Feld- und Quellencharakteristika des anomalen geomagnetischen Feldes hinsichtlich Möglichkeiten zur Bestimmung der Tiefenlage der magnetischen Krustenbasis

1963-1982: Research Scientist,

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1982 – 1991: Research Scientist

(Academy of Sciences, Institute for Polymer Chemistry, Teltow)

Since 1992: Senior Scientist

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### MALLS (Multi Angle Laser Light Scattering):

The highly sophisticated MALLS instrument DAWN EOS of Wyatt (USA) is normally equipped with a flow cell for use in chromatographic studies. The scattering intensity is simultaneously registered at 18 scattering angles and can be recorded along time for a huge number of slices. The time interval can be selected from 0.125 seconds upwards.

In principle, this instrument could also be used for batch measurements. However, an index-matching bath is not provided. Moreover, test studies with the recommended simple vial revealed that a lot of reflected light falsifies the measured scattering intensities. The scattering cell cannot be positioned in a reproducible way eliminating the strange light. We (cooperation with Herbert Dautzenberg) solve the problem using a special model of an index-matching bath, normal quartz glass light scattering cuvettes and a cover plate with bore to position the cuvette. The special bath was manufactured by Hellma according to our instructions. An attenuation filter to lessen the laser beam offers an additional extension of the measuring range. Calibration and normalization of the detection diodes can be carried out with high precision.

### Capabilities:

**Fig. 1** demonstrates the general capabilities of our equipment enabling the investigation of time dependent structure formation processes. The graphs show the reactions of a PEL (polyelectrolyte complex) solution to addition of salt.

The 3D-plot (**Fig. 1d**) and the plot of the scattering intensity for one angle (**Fig. 1a**) qualitatively show the kinetics of the process. After interpretation of the scattering curves for single slices /single time points, plots of the molecular parameters vs. time can be produced immediately. As an example **Fig. 1b, c** are given, using traditional interpretation procedures.

For particle sizes around or above 100 nm, more sophisticated algorithms of data interpretation are required. Respectively, special software was developed allowing to import the MALLS-data into our SLS-interpretation application.

This system offers additional procedures, especially a model interpretation using the entire angle range of the scattering curves [1]. Such a scaled interpretation yields results about the molecular parameters, polydispersities and structure densities. Moreover, the system offers the consideration of bimodal systems.

In this way, a large variety of time-dependent structural changes can be investigated. The advantage of the very high registration frequency of MALLS allows studying fast processes too.

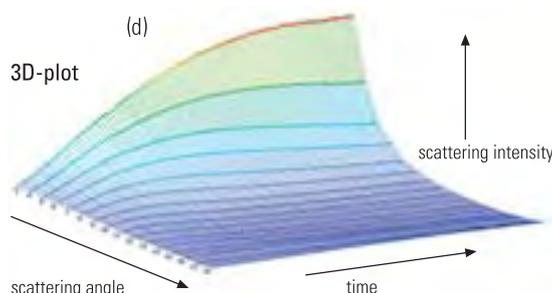
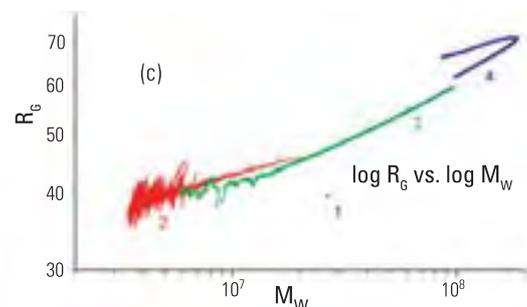
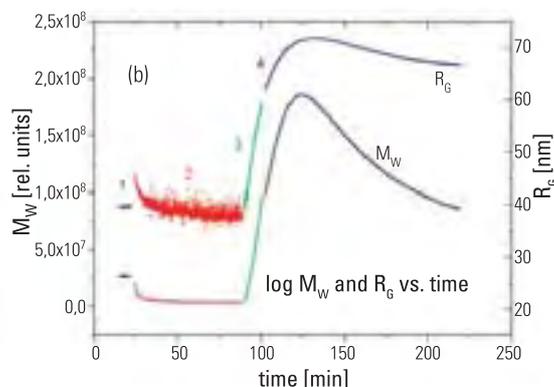
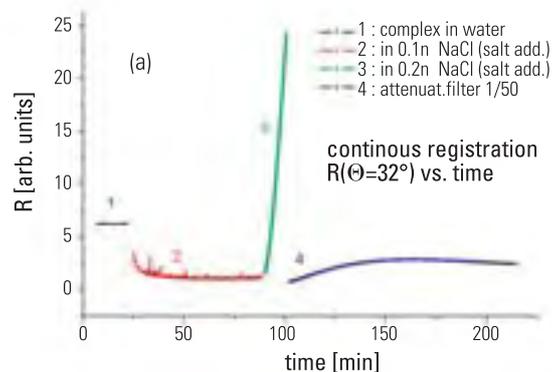


Fig. 1: MALLS of a PEL-complex,  
a: scattering intensity of one angle vs. time,  
b: molecular mass and radius of gyration vs. time,  
c: double logarithmic plot  $R_g$  vs.  $M_w$ ,  
d: 3D-plot

### Example:

We studied the dissolution of highly aggregated PEL particles formed in water after addition of salt [2]. The complex formation in pure water results in large highly aggregated complex micelles with an aggregation number of several thousand macromolecules. Mixing two polyelectrolyte components, a bimodal system is obtained. The first component is given by the complex micelles with a charge stoichiometry near 1:1, the second component consists of the excess free polyelectrolyte. The addition of salt allows a polyelectrolyte exchange reaction between the free polyelectrolyte chains in the solution and the aggregated particles. This leads to a redistribution between the short (deficient) and the long (excess) chain components resulting together with structural rearrangements in the decrease of the aggregation level and eventually in a monomodal system of "soluble" complex particles.

In order to investigate such a transition of a PEL structure from highly aggregated particles to "soluble" complexes of the molecular level, MALLS studies were performed. The time series of scattering for one angle ( $90^\circ$ ) was used for the study of the process kinetics.

The redistribution rate increases with increasing salt concentration in the solution. It decreases with an increasing mixing ratio (the ratio between the charges in deficiency and in excess in the mixture of two polyelectrolytes) and increases with a higher concentration of polyelectrolytes in solution. An interesting fact is that the dependence of the rate on the polymer concentration weakens with increasing salt concentration in the solution (Fig. 2).

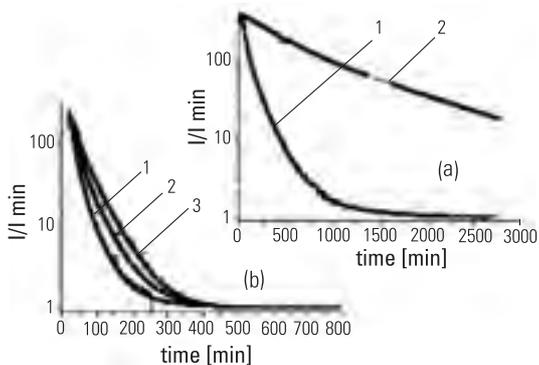


Fig. 2: Relative scattering intensity ( $\Theta=90^\circ$ ) as a time function for different polymer concentrations 1-3 ( $10, 5, 2 \cdot 10^{-4} M$ , in 0.01N (a), 0.02N (b) NaCl

To explain this fact structural changes were studied. Scattering curves of the system corresponding to different times after the process start have been analyzed by scaled interpretation. Fig. 3 shows that in the small angle range the curvature of the scattering curves increases only slightly indicating a slight increase of the dimensions of the aggregate particles. In the wide angle range, the difference between the experimental curves and theoretical ones increases. This indicates an increase of the fraction of small particles of soluble complexes. The changes in the intensity correspond mostly to the changes of the fraction of the aggregates in the solution and not to the changes in their mass. DLS (dynamic light scattering) studies confirm these results. The experimental data allows explaining the mechanism of aggregate transformation as a two step process. In a first step, the free polyelectrolyte chains in excess remove the short chain component from the particle via a polyelectrolyte exchange reaction. In the second step, the aggregated particle is destroyed by the osmotic pressure which increases with the increasing stoichiometry of the aggregate particle.

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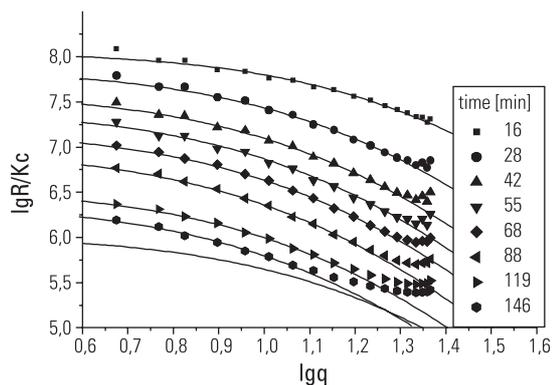


Fig. 3: Experimental and theoretical scattering curves for a PEL in 0.2N NaCl for different times

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## Modern Methods of Light Scattering



Static and dynamic light scattering are important methods for the characterization of macromolecular materials. The target of the research is to extend and apply these methods to problems specific to colloids and interfaces.

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Thesis: Stress Optical Behaviour of Liquid Crystalline Elastomers

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Thesis: Investigation of the Nematic Wetting Layer in an Isotropic Liquid Crystal by Evanescent Light Scattering

**1997-1998:** Postdoc  
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**1998-2000:** Postdoc  
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**Since 2000:** Group Leader  
(Max Planck Institute of Colloids and Interfaces, Gölml)

### Ellipsometric Scattering

A special feature of colloidal materials is their large surface due to the fine dispersion of matter. Combining light scattering with polarization optics common to ellipsometry results in a new experimental technique capable to access this characteristic surface.

The high resolution of classical ellipsometry is achieved by measuring the amplitude ratio  $\tan(\psi)$  and especially the relative phase shift  $\Delta$  of two polarization modes  $E_p$  parallel and  $E_s$  perpendicular to the plane of reflection (Fig. 1a). Here, the phase shift arises from the reflection at a planar interface with a refractive index profile, e.g. a two-step profile with indices  $n_1$ ,  $n_2$  and  $n_3$ . Similarly, in a scattering experiment (Fig. 1b), the amplitude ratio and relative phase shift of two polarization modes  $E_p$  parallel and  $E_s$  perpendicular to the scattering plane is determined by the refractive index profile of the scattering particle.

The availability of a correlator for dynamic light scattering immediately gives access to the dynamics of the refractive index profile, i.e. breathing modes of the particle. Another important aspect is the effect of sample polydispersity, where ellipsometric scattering allows distinguishing the scattering of an average particle (coherent scattering) from scattering caused by deviations from the average size (incoherent scattering).

As an example, Fig. 2 shows experimental data and corresponding fits for the characterization of coated colloid particles.

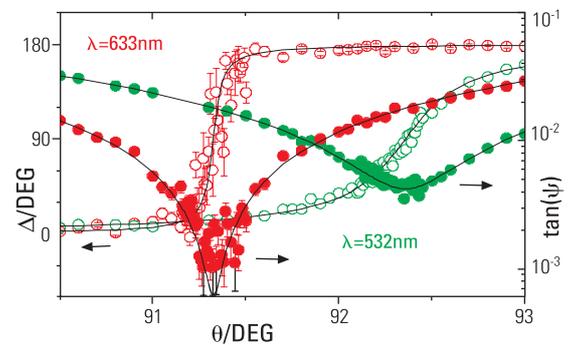


Fig. 2: Ellipsometric scattering data from PMMA particles with PNIPAM coating in water with 190 nm core diameter and 20nm surface layer at the temperature 32 °C

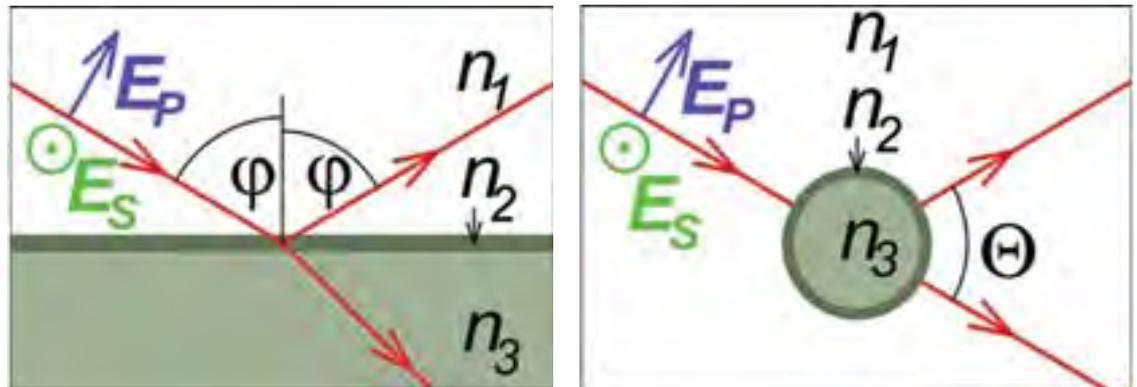


Fig. 1: Comparison of reflection ellipsometry (a) and Scattering ellipsometry (b).

### Procedures of Interface Light Scattering (PILS-Project)

A liquid-liquid interface is a soft system with many possible fluctuations. It is possible to monitor these fluctuations by reflecting a light beam at the interface, as displayed in **Fig. 3**. The polarization analysis of the reflected beam (E) yields the interface thickness (ellipsometry), while small angle scattering (C) is sensitive to capillary waves. For total internal reflection, the evanescent wave with exponentially decaying field profile (depicted in blue in **Fig. 3**) defines a scattering volume with a thickness comparable to the wavelength of light,  $\lambda$ . Scattering of the evanescent wave (S) reflects structure and dynamics close to the interface.

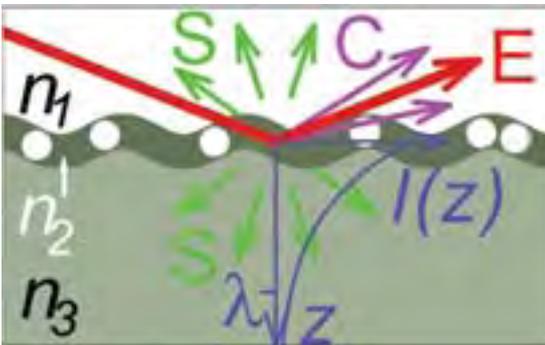


Fig. 3: Characterization of an interface with light (see text).

A new setup combining ellipsometry, evanescent light scattering and capillary wave detection is under construction. Planned experiments deal with 2D-diffusion of colloids in the interface under the effect of capillary waves and dynamics of exchange processes through the interface.

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## Adsorption Properties of Surfactants at Fluid and Solid Interfaces



### Aims:

Investigations on the true adsorption properties of surfactants, including lung surfactant and solvosurfactants. Elucidating surfactant functionality in terms of surfactant structure, charge and counterion size. Development of a generally applicable method for swift foam characterization and of a method for surfactant adsorption at solid/liquid interfaces.

### Results:

Systematic investigations on basic and applied adsorption properties of amphiphiles at air/water and solid/liquid interfaces have been continued by strictly keeping the requirements of "surface-chemical purity" (scp) to avoid artefacts due to surface-active trace impurities [1]. The surfactants investigated include simple and more complicated structures.

### 1. Basic Research

#### 1.1 Novel Surfactants

Novel surface-active di-*n*-alkylaldonamide derivatives (sugar surfactants) were synthesized from biologically available materials. Their adsorption behavior is quite unusual. Unlike ordinary *n*-alkyl surfactants the amphiphiles cross-sectional area and the surface interaction parameter show a strong increase with rising alkyl chain length, but abruptly decrease after having reached a certain medium chain length. These thermodynamic results suggest that for the longer chain homologues an abrupt deviation from that surface conformation occurs which is met for the lower numbered homologues: one alkyl chain is protruded upright from the boundary while the second one remains flat [2]. This hypothesis is supported by HyperChem Computer Simulations.

#### 1.2 Phase Transition

Investigations of surface potential and surface tension of the homologous series of the sugar surfactants *n*-alkyl- $\beta$ -D-glucopyranosides revealed a first order phase transition so far unknown at air/water interfaces. Unlike known phase transitions, it occurs at negligible surface interaction [3]. It seems to be induced by changes in the water structure of the interfacial layer.

#### 1.3 Counterion Effect

Equilibrium surface tension of anionic *n*-decylsulfates for various monovalent alkali counterions revealed that the surface activity of the scp decylsulfates significantly decreases with decreasing hydrated size of the counterion. By the assumption that the counterions penetrate the Stern layer where the surfactant head groups are adsorbed an adsorption model was developed taking into account that head group and counter ion have a finite size ("surface exclusion effect"). Good correlation between the relative counter ion size in the Stern layer, the effective radius and the area excluded by the adsorbed counter ion was obtained [4]. The resulting cross-sectional areas of the adsorbed decylsulfates for the various counterions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  are in good agreement with those measured by neutron scattering.

#### 1.4 Solvo-Surfactant

Investigations on solvosurfactants using Dowanol DPnB (dipropylene glycol *n*-butyl ether) were performed to learn why solvosurfactants have solvent and surfactant properties as well. First results with scp-solutions suggest that this effect is obviously brought about by trace impurity components the adsorption properties (molecular structure) of which are rather different from that of the main component [5].

#### 1.5 Lung Surfactant

The high-performance purification apparatus developed by us previously was applied to bronchoalveolar lavage (BAL) to isolate the native surface film of the lung surfactant system. By this technique the surface-active material is aspirated from the solution surface. The aspirated solutions, the original BAL fluid pool as well as the residual bulk phase were analyzed for the total protein, total phospholipids and phospholipid subclasses. Generally, the protein and the phospholipid concentrations in the aspirated solutions were two to three times higher than in the BAL fluid. These results prove that proteins and different phospholipids are an integral part of the surface film of the BAL fluid. Moreover, this technique provides a new advantageous possibility for the isolation of lung surfactant.

Measuring surface pressure and applying quantitative Brewster Angle Microscopy (BAM) the inhomogeneous nature of the surfactant film with three distinct different morphological phases was observed. On the basis of these results a mechanism of the lung stabilizing mechanism has been proposed that is in line with surfactant behavior at interfaces and the morphological structure of the lung surfactant (Fig. 1) [6].

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**1963:** Diploma, Inorganic Chemistry (Ernst-Moritz-Arndt-Universität Greifswald)

Thesis: Zur Darstellung von Lithium-phthalocyanin-chromat(0)

**1970:** PhD, Physical Chemistry

Thesis: Untersuchungen zur Bestimmung der Elastizität von

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**1972:** Group Leader (Zentralinstitut für Organische Chemie of the

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**1980-1982:** Teaching Assignment (Technical University of Dresden)

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**1992:** Facultas docendi (Martin-Luther-Universität Halle-Wittenberg)

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**1999:** Guest Lecturer

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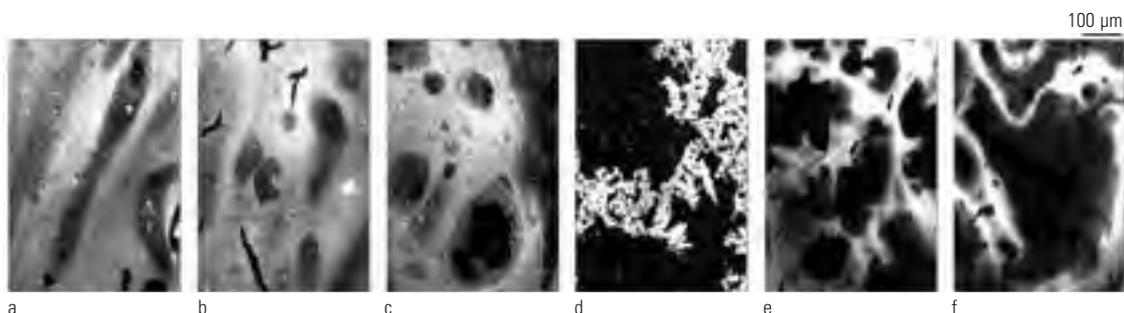


Fig. 1 BAM images of different stages of lung surfactant during spontaneous adsorption

### 1.6 Adsorption Isotherms of Surfactants on Solid Phases

The determination of surfactant adsorption on solid surfaces by the old batch-technique is very complicated and requires a great time exposure. In order to improve this method a new technique based on dynamic frontal high performance liquid chromatography using ELS- and/or MS-detection was developed. The limit of detection is 5 and/or 1  $\mu\text{g/ml}$  of surfactant, also in the presence of partially soluble substances and contaminations. Additionally, the MSD can discriminate between soluble substances and surfactant that increases the specification of the method considerably. The method is applicable for insoluble and partially soluble substances.

## 2. Applied Research

The development of a new, generally applicable method for swift characterization of foam stability was continued. The advantage of this pneumatic method is that the foam parameters by means of which stability is characterized are related to well-defined boundary conditions of the system [7]. A patent about this method has been submitted [8]. Investigations are now in progress to describe the dynamic foam behavior and the new foam parameters concentration dependence quantitatively. To get further insight into the foam stabilizing mechanism the relevant foam parameters are compared with the structure of the surfactants, their adsorption and bulk properties. In cooperation with our partner in Poland we look for a correlation between the behavior of a single foam bubble during its rise through a surfactant solution and its foam properties. Analysis of the high-speed camera pictures revealed an unknown periodically bouncing of the bubble when it meets the air/solution interface [9].

### Cooperations

- Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, Cracow, Poland
- Institute of Organic and Polymer Technology, Technical University of Wroclaw, Poland
- Royal Institute of Technology, Department of Surface Chemistry, Stockholm, Sweden
- Bundesanstalt für Materialforschung, Berlin, Germany
- Institute of Physical and Theoretical Chemistry, University of Regensburg, Germany
- Institute of Inorganic Chemistry, University of Würzburg, Germany
- Fraunhofer-Institut für Angewandte Polymerforschung, Golm, Germany
- Technische Fachhochschule Wildau

### External Funding

- BAYER-Project
- German Academic Exchange Service (DAAD)

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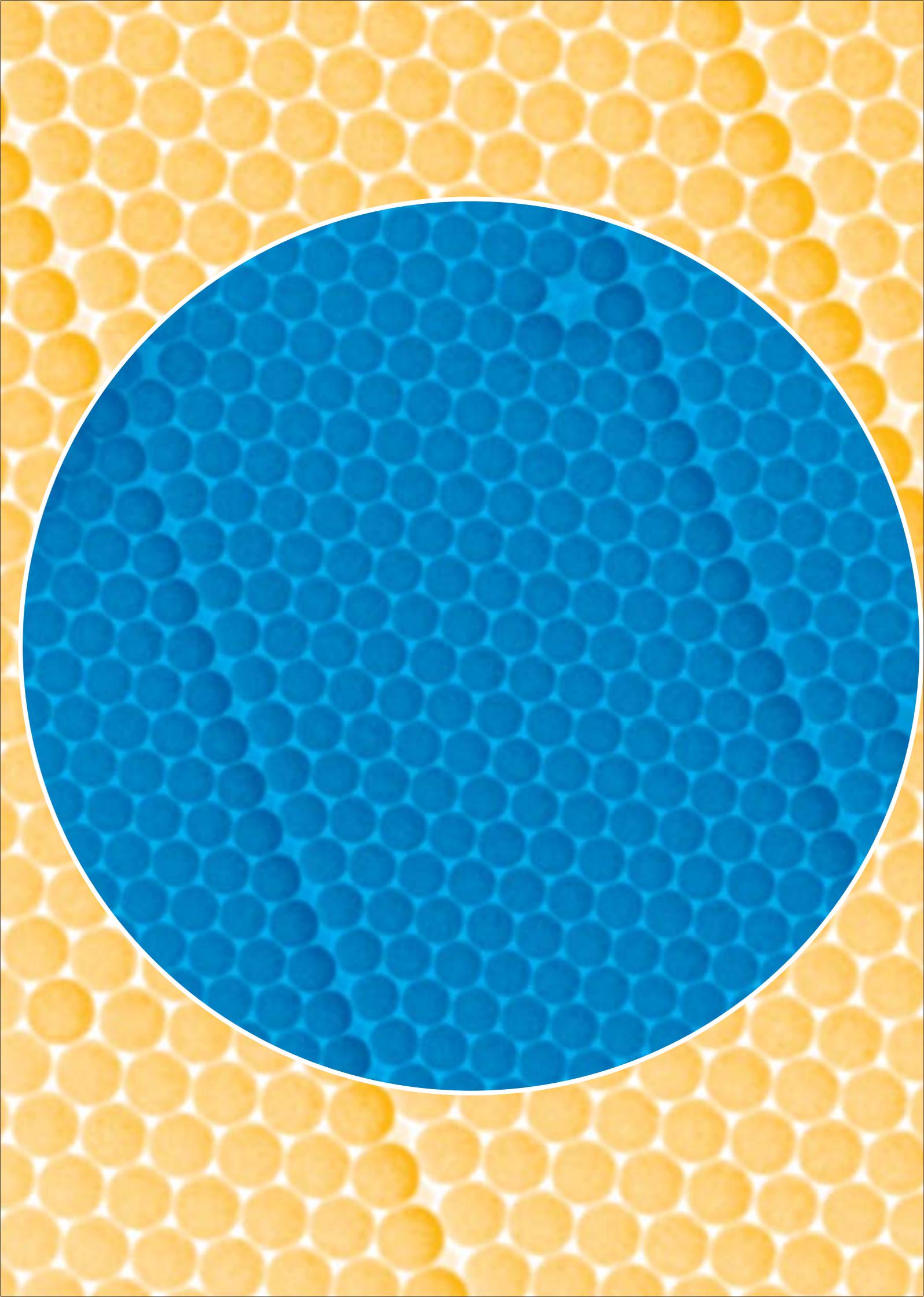
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- [4] Warszynski, P., Lunkenheimer, K., Czichocki, G.: Effect of Counterions on the Adsorption of Ionic Surfactants at Fluid-Fluid Interfaces (Alkali-decylsulfates). Langmuir 18, 2506-2514 (2002).
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- [7] Lunkenheimer, K., Malysa, K.: Simple and Generally Applicable Method of Determination and Evaluation of Foam Properties. J. Surfactant and Detergents 6, 69 (2003).
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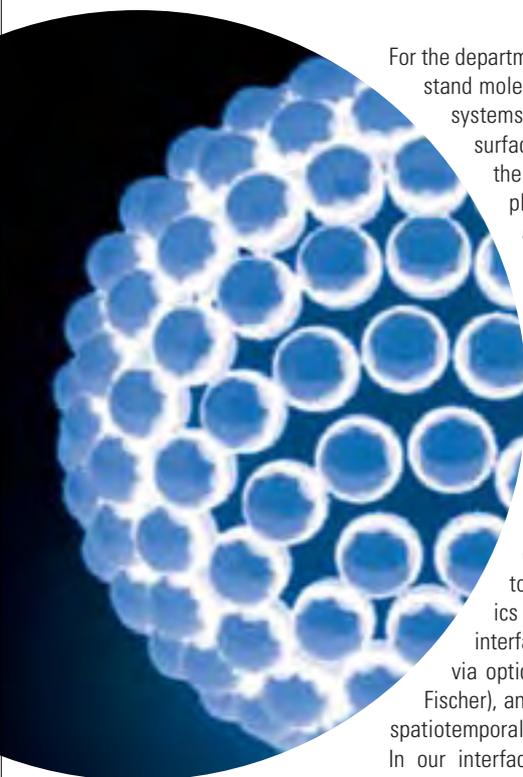


INTERFACES

# INTERFACES



## Research in the Department of Interfaces



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

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

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

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

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

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

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

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

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

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

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

## Interactions in Complex Monolayers



### Generic Phase Diagrams of Special Phospholipids

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

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

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

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

### Stepwise Collapse of New Silicon Polymer Films

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

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

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

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

[In cooperation with R. Klinger (Jena)]

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

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

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

### Interactions of Amyloid $\beta$ with Interfaces

[In cooperation with A. Thünemann (Golm)]

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

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

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

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

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1974: Diploma, Biophysics

(Lomonossov University of Moscow)

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

1981: PhD, Physical Chemistry

(Martin Luther University of Halle/S.)

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

1987: Habilitation, Colloid Chemistry

(Martin Luther University of Halle/S.)

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

1981-1982: Postdoc (Biological

Research Centre, Szeged, Hungary)

1982-1992: Research Scientist

(Institute of Physical Chemistry,

University of Halle/S.)

1992-1995: Research Scientist

(Institute of Physical Chemistry,

University of Mainz)

Since 1995: Group Leader

(Max Planck Institute of Colloids

and Interfaces, Golm)

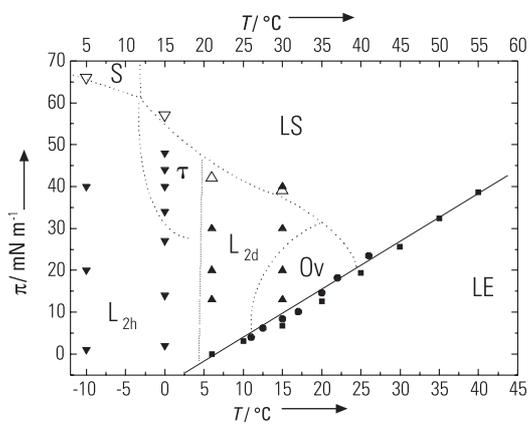


Fig. 1: Generic phase diagram of 1-O-hexadecyl-2-acyl-glycero-3-phosphocholines

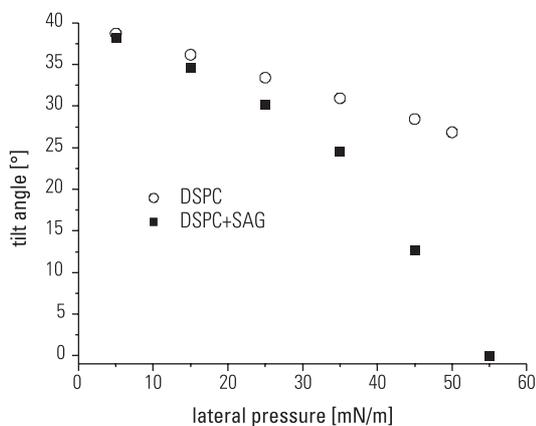


Fig. 3: Tilt angle as a function of film pressure at 20 °C for DSPC and for DSPC mixed with SAG, mimicking PI

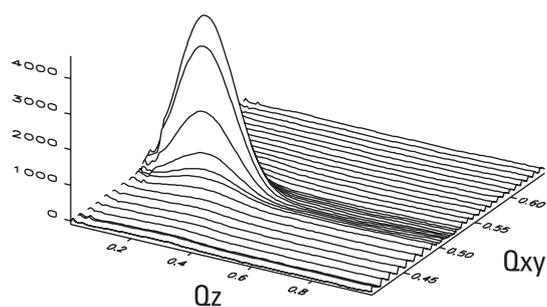
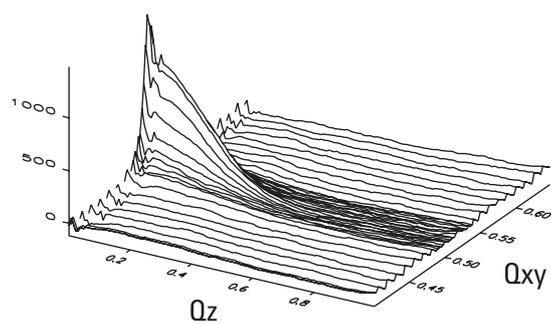


Fig. 2: Diffracted intensity as function of in-plane and out-of-plane scattering vector components  $Q_{xy}$  and  $Q_z$  at 0mN/m (top) and 10mN/m (bottom) for a cyclolinear polysiloxane monolayer

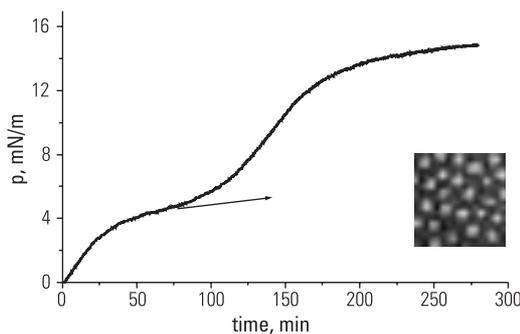


Fig. 4: Adsorption kinetics of  $A\beta$  and BAM image (right)

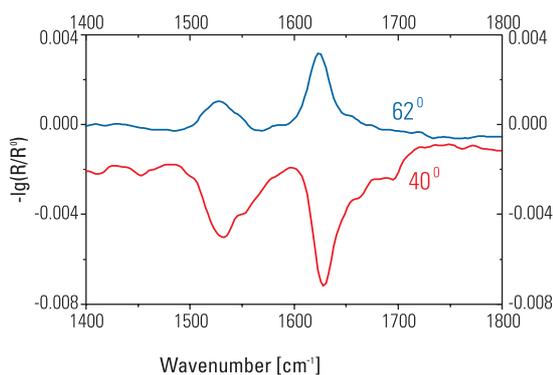


Fig. 5: FT-IR spectra at the air/water interface for  $A\beta$  monolayers using p-polarized light at different angles of incidence

#### Key Publications:

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

## Analysis – Synthesis – Purification of Amphiphiles



### Effect of Counter Ions on the Behavior of Soluble Anionic Surfactants

#### Aims:

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

#### Results:

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

Thermodynamics of micelle formation of anionic surfactants was investigated by using isothermal titration calorimetry (ITC). Highly purified decyl and dodecyl sulfates have been used to analyze the effect of counter ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>). Critical micelle concentration (cmc) and enthalpy of demicellization were systematically determined between 10 °C and 60 °C. The decrease of the cmc in the order Li<sup>+</sup>>Na<sup>+</sup>>K<sup>+</sup>>Cs<sup>+</sup> for a fixed chain length (**Fig. 2**) is related to the decrease of the degree of ionization of the –SO<sub>4</sub><sup>-</sup> M<sup>+</sup> bond. The electrostatic repulsions between ionic head groups prevent the aggregation but are progressively screened as the ionic character decreases with the size of the counter ion. Temperature changes cause large variations of ΔH<sub>mic</sub> and ΔS<sub>mic</sub>, whereas ΔG<sub>mic</sub> remains almost constant. The enthalpy of micellization decreases strongly with increasing temperature (**Fig. 3**) passing through zero (endothermic to exothermic). At a given temperature, ΔH<sub>mic</sub> decreases with the size of the counter ion. This finding is directly related to the energy required to overcome the electrostatic repulsion between head groups.

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

#### Aims:

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

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

#### Results:

The results concerning the distribution of nonionic surfactants in the water/hexane system are consistent with the partial lipophilic character of the polyoxyethylene chain and with the strong influence of the carbon chain on the surfactants properties. K<sub>p</sub> decreases strongly with the temperature. In the concentration range below the cmc the distribution coefficient is independent of concentration. With increasing number of EO groups the temperature dependence of K<sub>p</sub> becomes steeper. A ring structure in the molecule corresponds to effectively four CH<sub>2</sub> groups in an aliphatic chain (**Fig. 4**).

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**Dr. Gunther Czichocki** 06.04.1938

**1964:** Diploma, Chemistry

(Humboldt-Universität Berlin)

Thesis: Synthesis and sulfation

of Ricinolic- and 12-Hydroxystearic

acid-n-alkyl esters of the chain

length C1-C6

**1968:** PhD, Chemistry

(Humboldt-Universität Berlin)

Thesis: Synthesis of anionic surfactants

by sulfation of N-substituted

amides of 12-Hydroxyoctadecanoic acid,

12-Hydroxyoctadecenoic-(9)-acid and

11-Hydroxyundecanoic acid

**1981-1982:** Study of Colloid Science

(Technische Universität Dresden)

**1964-1991:** Central Institute of Organic

Chemistry of the Academy of Sciences

**Since 1992 :** Group Leader

(Max Planck Institute of Colloids

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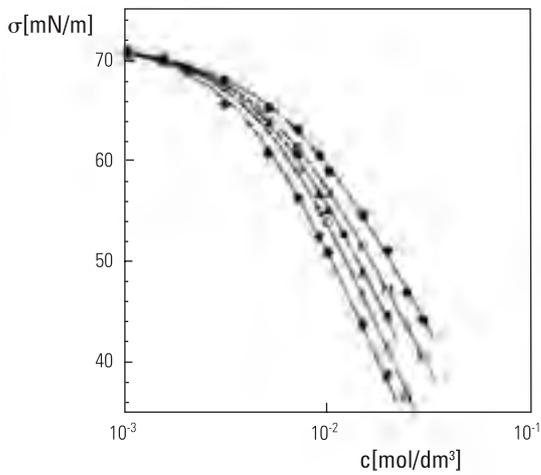


Fig. 1: The dependence of the surface tension of LiDS – black circles, NaDS – white squares, NH<sub>4</sub>DS – black triangles, KDS – white circles and CsDS – black diamonds, on their concentration. Lines represent fits of the theoretical model of adsorption of ionic surfactants to experimental data.

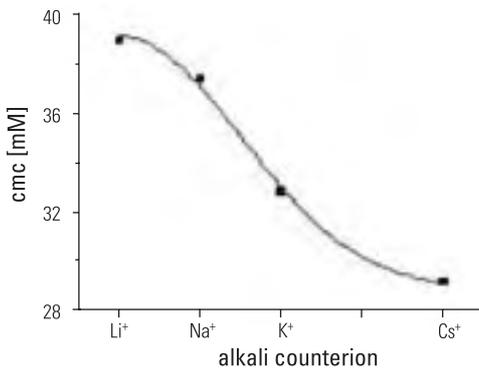


Fig. 2: cmc of decylsulfates versus alkali counter ion

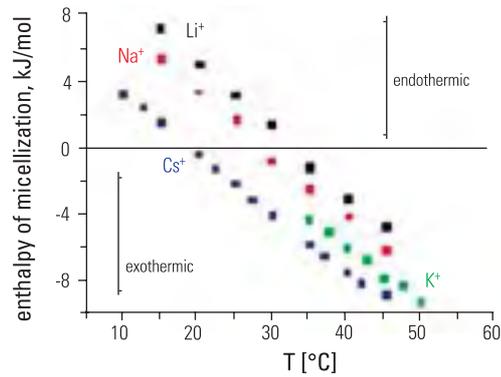


Fig. 3:  $\Delta H_{mic}$  of decylsulfates with different alkali counter ions versus temperature

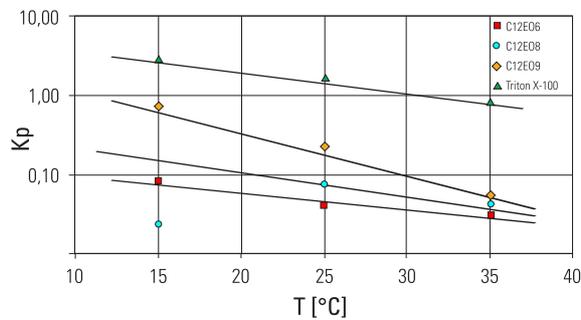
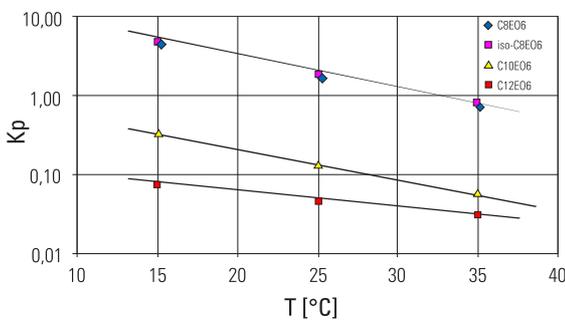


Fig. 4: Partition coefficients at the hexane / water interface of selected  $C_nEO_m$  as a function of temperature of  $T$ ;  $K_p(T) = \frac{C_W}{C_H}$

#### Key Publications:

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

## (QUASI) PLANAR INTERFACES - FLUID INTERFACES

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



### Aims:

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

### Results:

#### **Modulation Crack Growth and Crack Coalescence upon Langmuir Monolayer Collapse**

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

#### **Shapes of Langmuir Monolayer Domains in Confined Geometries**

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

#### **Wetting in Asymmetric Quasi-2 Dimensional-Systems**

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

#### **Cavitation of Langmuir Monolayers**

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

#### **Electrophoretic Relaxation Dynamics of Domains in Langmuir-Monolayers**

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

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

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**1989:** Diploma, Theoretische Physik  
(Technical University of Munich)

Thesis: Einfluss der Dipolwechselwirkung auf dynamische Messgrößen in Ferro- und Antiferromagneten

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

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

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

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

**1999:** Habilitation, Experimental Physics (University of Leipzig)

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

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

### Equilibrium Size of Circular Domains in Langmuir-Monolayers

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

### Liquid Crystalline and Solid Stripe Textures in Langmuir Monolayers

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

### Stability Criteria for 2 Dimensional Wetting in Monolayers

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

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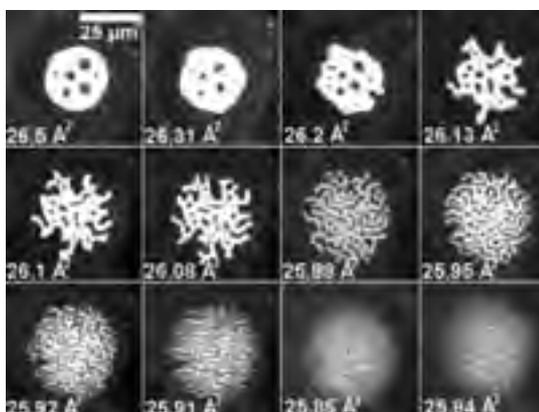


Fig. 1: Shape instability of a liquid 2D droplet. The circular droplet shape changes toward a labyrinth pattern upon confinement of the droplet.

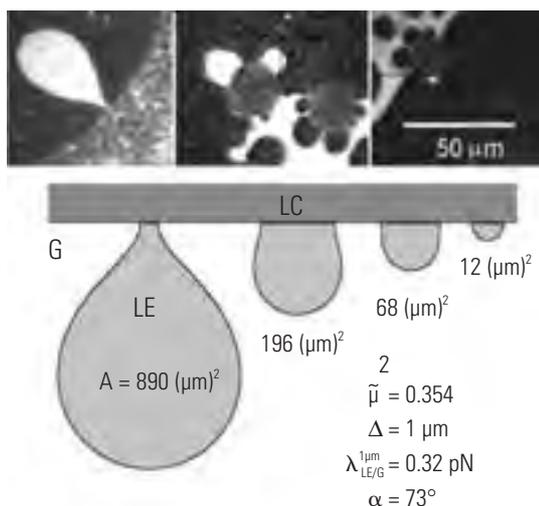


Fig. 2: Shape of electrostatically deformed pendant droplets, experiment versus theory

### Key Publications:

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

# (QUASI) PLANAR INTERFACES - FLUID INTERFACES

## Thermodynamics, Kinetics and Dilational Rheology of Interfacial Layers



### Aims:

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

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

### Results:

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

### Systematisation of Equations of State

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

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

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

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

$\Delta G^0 = \Delta G_{\text{CH}_2}^0 \cdot n_c + \Delta G_{\text{P}}^0$ . The increment values of standard free energy per methylene unit  $\Delta G_{\text{CH}_2}^0$  for various ionic and non-ionic surfactants vary between -2.6 kJ/mol and -3.3 kJ/mol. The free energy increment for non-oxethylated polar head groups  $\Delta G_{\text{P}}^0 = -4.25$  kJ/mol does not significantly depend on surfactant nature. **Fig. 1** summarizes the experimental data of the adsorption constant  $b$  on  $n_c$  for a large number of surfactants for non-ionic and  $\alpha = 1/2$  for ionic surfactants, and  $\rho \approx 55.6$  [mol H<sub>2</sub>O/l]. For the non-ionic and amphoteric surfactants the lines 1 and 2 correspond to  $\Delta G_{\text{CH}_2}^0 = -(2.6 \div 3.0)$  kJ/mol, and for ionic surfactants the lines 3 and 4 correspond to  $\Delta G_{\text{CH}_2}^0 = -(2.6 \div 3.0)$  kJ/mol, i.e. they agree with the generally accepted increments for non-ionic surfactants. For oxethylated non-ionic surfactants (C<sub>n</sub>EO<sub>8</sub>, line 5) and ionic surfactants (C<sub>n</sub>EO<sub>2</sub>SO<sub>3</sub>Na, line 6) we have  $\Delta G_{\text{CH}_2}^0 = -2.86$  kJ/mol and -3.3 kJ/mol, respectively.

### Surface Thermodynamics of Surfactant Mixtures

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

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

which can be rewritten into a simple form (1)

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

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

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

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

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

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

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Thesis: Fredholm Operators

**1977:** Research Stay

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**1978:** PhD, Physical Chemistry (Academy of Sciences, Berlin)

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

**1988:** Habilitation, Physical Chemistry (Academy of Sciences, Berlin)

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

**1990/91:** NCERC Fellow

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**Since 1992:** Group Leader

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**2002:** Research Stay

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

### Dilational Elasticity of Adsorption Layers

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

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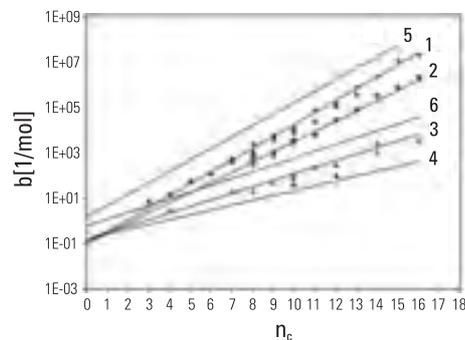


Fig. 1: Adsorption equilibrium constant  $b$  as a function of  $n_c$  for various surfactants: ( $\blacktriangle$ )  $C_nOH$ ; ( $\diamond$ )  $C_n(OH)_2$ ; ( $\triangle$ )  $C_nO_2H$ ; ( $\blacklozenge$ )  $C_nDMPO$ ; ( $\blacksquare$ )  $C_nBHB$ ; ( $\square$ )  $C_nPIP$ ; ( $\times$ )  $C_nEO_8$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

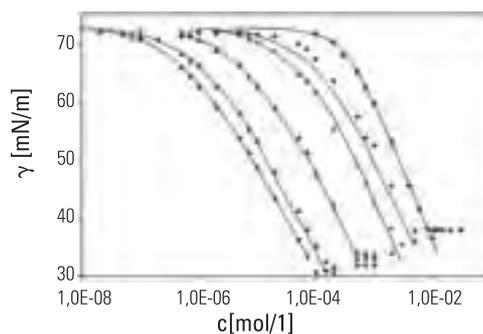


Fig. 2: Surface tension isotherms for  $C_{10}EO_5$  ( $\diamond$ ), SDS in 0.01M NaCl ( $\square$ ) and their mixtures in 0.01M NaCl with ratios 1:1 ( $\triangle$ ), 1:10 ( $\blacktriangle$ ), 1:100 ( $\circ$ ) and 1:500 ( $\bullet$ ), solid lines are theoretical isotherms

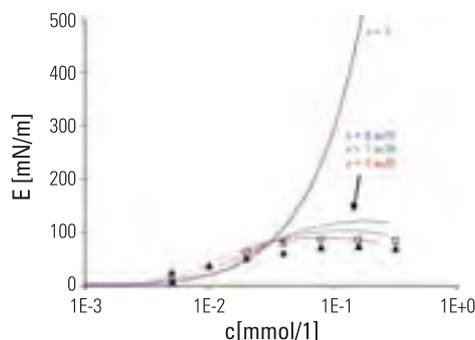


Fig. 3: Comparison of experimental surface dilational elasticity of  $C_{12}DMPO$  solutions at  $f > 400$  Hz (symbols, data from literature); Theoretical dependencies were calculated for different values of  $\varepsilon$ , the thick solid line refers to  $\varepsilon = 0$

### Key Publications:

- [1] Fainerman, V. B., Miller, R. and Möhwald, H.: General Relationships of the Adsorption Behaviour of Surfactants at the Water/Air Interface. *J. Phys. Chem.*, 106, 809-819 (2002).
- [2] Fainerman, V. B. and Miller, R.: Simple method to estimate surface tension of mixed surfactant solutions. *J. Phys. Chem. B*, 105, 11432-11438 (2001).
- [3] Fainerman, V. B., Miller, R. and Kovalchuk, V. I.: Influence of compressibility of adsorbed layers on the surface dilational elasticity. *Langmuir*, 18, 7748-7752 (2002).

# Molecular Organization in Soluble Monolayers and Functional Films



### Aims:

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

### Results:

#### Wetting

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

#### Nonlinear Optical Devices:

(Collaboration with University of Potsdam, S. Schrader and the University of Göteborg)

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

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

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

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

#### Soluble Surfactants

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

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

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

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

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

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**1988:** Diploma, Chemistry

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

**1991:** PhD, Chemistry

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Thesis: Scaling and adsorption

studies of Block-copolymers

**1991-1993:** Postdoc

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**Since 1994:** Group Leader

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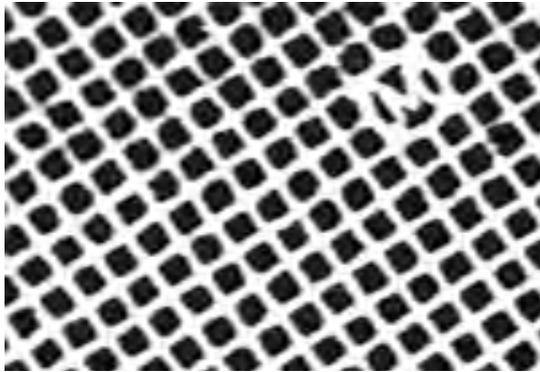


Fig. 1: Wetting pattern generated by a cis-trans motif within a monolayer. The writing process is fully reversible.

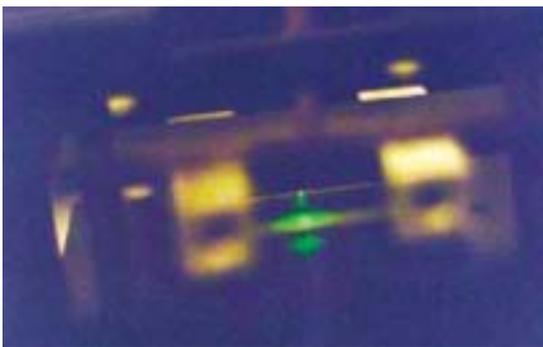


Fig. 2: Efficient conversion in a slab waveguide with an inverted waveguide structure. For the switching experiment the device is operated close to phase mismatch

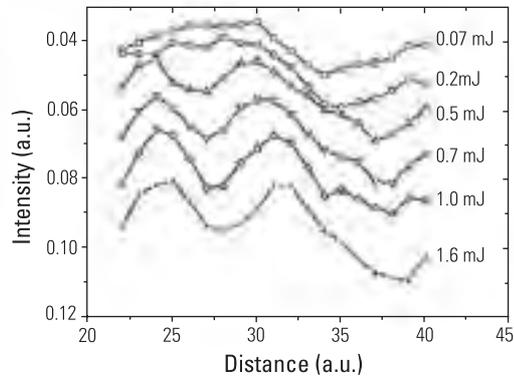


Fig. 3: Interference fringes measured in a MZ interferometer with the inverted waveguide structure in one arm. This experiment yields the nonlinear phase shift.

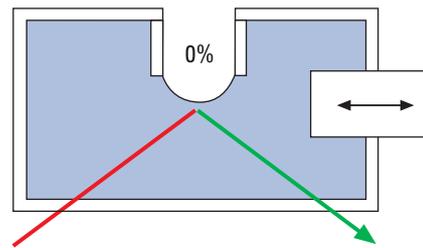


Fig. 4: Oscillating bubble combined with SHG in total reflection mode

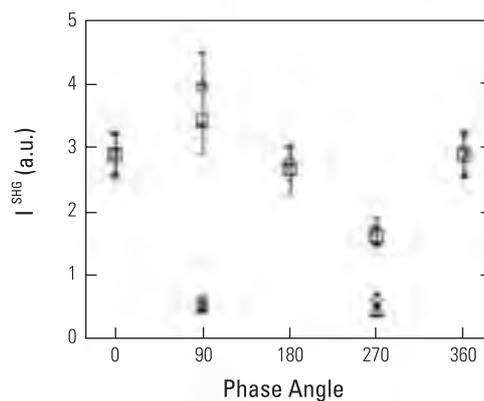


Fig. 5: SHG response as a function of the phase difference between bubble and laser light system

#### Key Publications:

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

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

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

## Thin Liquid Films



### Aims:

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

### Results:

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

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

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

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

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

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Thesis: Pulsed gas ion laser

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

1971-1978: Research Scientist

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

1979-1991: Group Leader

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

Since 1992: Group Leader

(Max Planck Institute of Colloids and Interfaces, Golm)

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

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#### Key Publications:

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

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

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

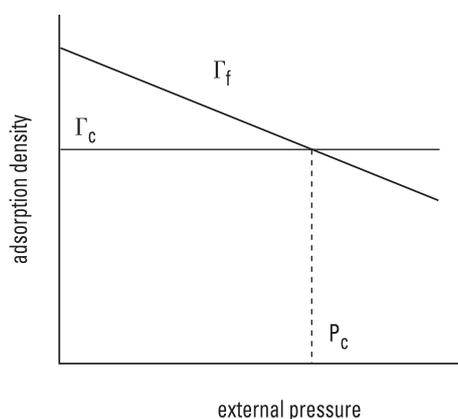


Fig. 1: Foam film rupture at a critical pressure  $p_c$

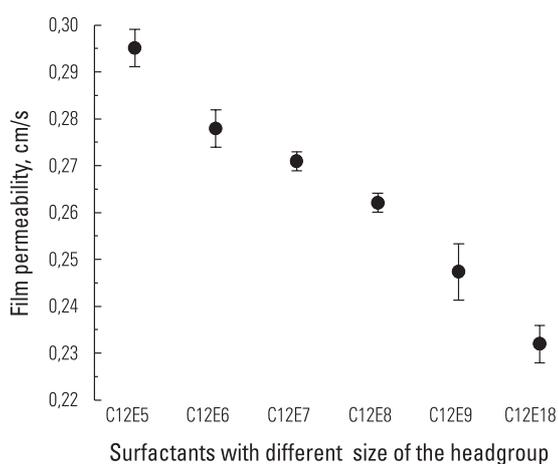


Fig. 2: Gas-permeability of foam films depending on the number of EO-groups in the stabilizing oxethylated dodecanole

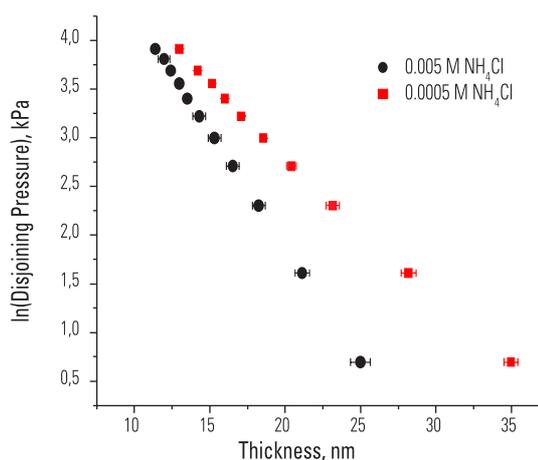


Fig. 3: Disjoining pressure of a perfluoro octane surfactant as a function of film thickness for different concentrations of  $NH_4Cl$

## Supramolecular Organization of Amphiphilic Monolayers



### Aims:

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

### Results:

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

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

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

The following theoretical work has been performed:

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

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

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

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

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

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

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

D. Vollhardt, V. B. Fainerman, O. Grigorieva, F. Liu, N. Nandi, N. M. Kovalchuk, V. I. Kovalchuk, S. Siegel, Yu. B. Vysotsky  
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**Dieter Vollhardt** 26.08.1937

**1961:** Diploma, Chemistry  
(University of Greifswald)

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

**1966:** PhD, Physical Chemistry

(Humboldt-University Berlin)

Thesis: Desorption studies of surfactants using a new diffusion-kinetic system

**1966-1971:** Group Leader

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

**1972-1991:** Group Leader (Central

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**1982:** Habilitation

(Academy of Sciences, Berlin)

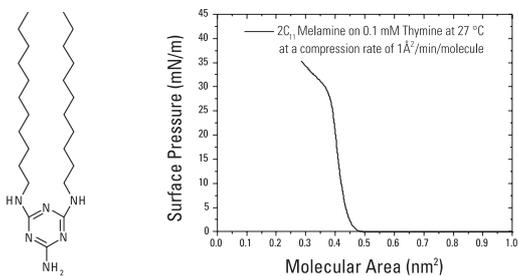
Thesis: Studies of structure and molecular interactions in amphiphilic monolayers at the air/water interface

**1992:** Group Leader

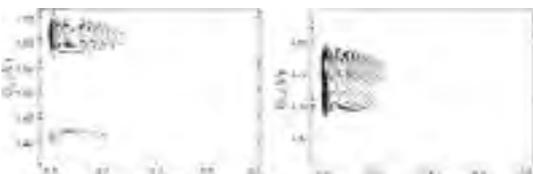
(Max Planck Institute of Colloids and Interfaces, Golm)

**1999:** Professor

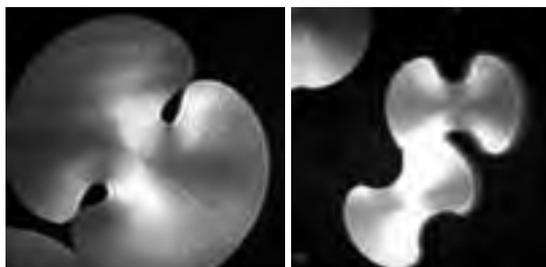
(University of Potsdam)



Formula and  $\pi$ -A isotherm



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



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

Fig. 1: Molecular recognition of dissolved thymine

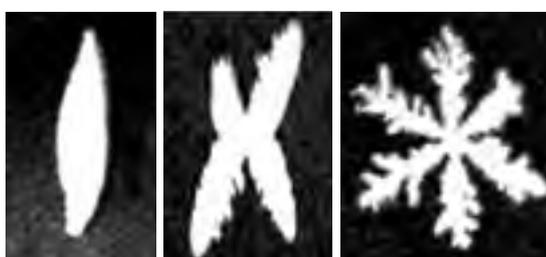


Fig. 2: Representative domains of 9-hydroxy-palmitic acid monolayers at 5, 10 and 15  $^\circ\text{C}$

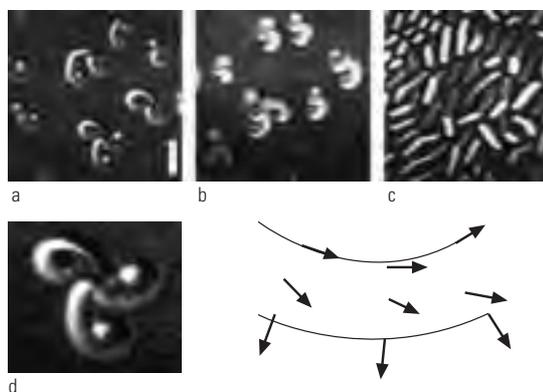


Fig. 3: BAM images of (a) D- (b) L- and (c) DL-DPPC domains; an enlarged D-DPPC domain in (d), and changes in molecular director within an arm of the triskelion in (e)

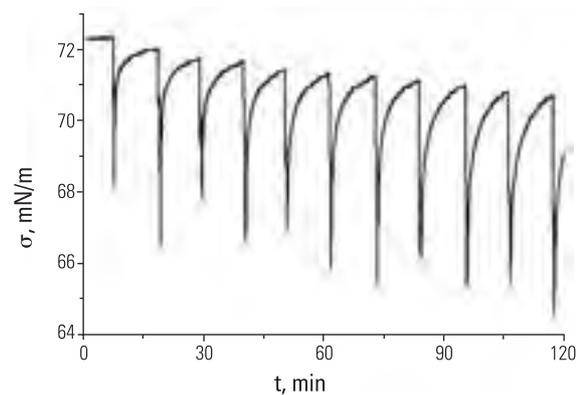


Fig. 4: Surface tension  $\sigma$  versus time, Auto-oscillation in octanol-water system, 9 mm capillary immersion depth; 46 mm cell diameter

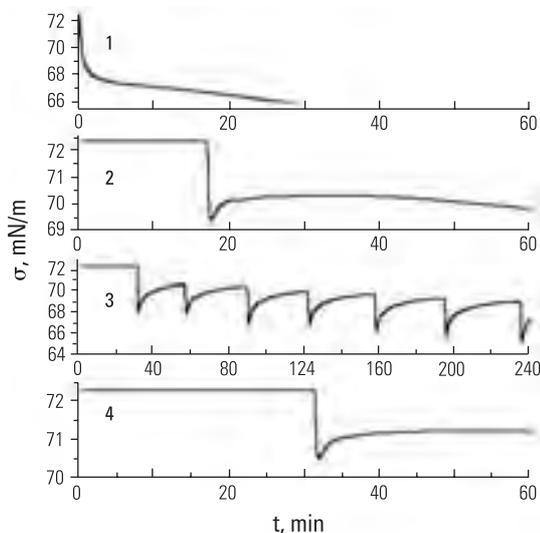


Fig. 5: Surface tension  $\sigma$  versus time. Oscillation behavior in dependence on system geometry. Constant cell diameter of 40 mm (1-3) and larger (60 mm) (4); immersion depth is small (1 mm) (1), medium (6 mm) (2), large (8 mm) (3) (4).

**Key Publications:**

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

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

## Rheological Properties of Fluid Interfaces



### Aims:

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

### Results:

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

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

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

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

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

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

Thesis: Berechnung eines un stetigen Eigenspannungsproblems

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

Thesis: Ein Näherungsverfahren zur Lösung von Spaltbeugungsproblemen

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

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

**Since 1992:** Group Leader

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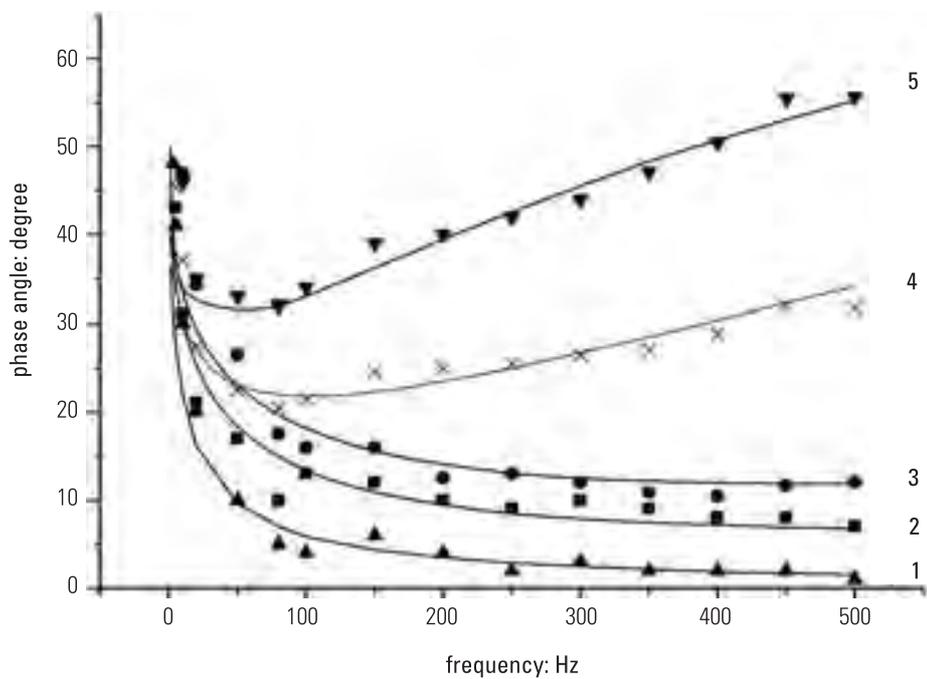
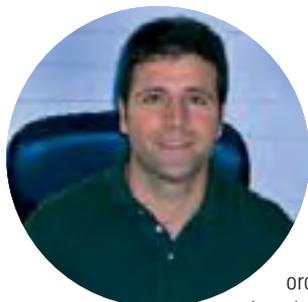


Fig 1: Phase angle of the surface dilatational modulus as a function of frequency for mixed  $5 \cdot 10^{-3}$  M SDS/x mol% dodecanol solutions: (1/ ▲) x=0.4 mol% ( $f > 100$ Hz: pure elastic surface), (2/ ■) x=0.1 mol%, (3/ ●) x=0.06 mol%, (4/ ×) x=0.05 mol%, (5/ ▼) x=0 mol% (viscoelastic surfaces),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

**Key Publications:**

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

## Nanostructured Interfaces and Materials



### Aims:

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

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

### Results:

#### A. Preparation of Tailored, Functional Colloids

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

#### (i) Biocolloids.

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

#### (ii) Nanoparticle Functionalization.

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

#### (iii) Gold-Coated Spheres.

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

#### B. Advanced Materials from Coated Colloids

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

#### (ii) Macroporous Materials.

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

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1989: B. Sc. (Hon.),

Physical Chemistry (The University of Melbourne, Australia)

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

1994: Ph.D., Physical Chemistry

(The University of Melbourne, Australia)

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

1994-1996: Postdoctoral Fellow,

Division of Chemicals and Polymers

(CSIRO, Melbourne, Australia)

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

1999-2002: Group Leader

(Max Planck Institute of Colloids

and Interfaces, Golm)

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

### (iii) Biocatalytic Films.

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

### C. Multilayered Thin Films

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

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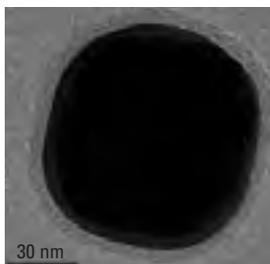


Fig. 1.: TEM micrograph of a gold nanoparticle coated with two layers of oppositely charged polyelectrolytes.

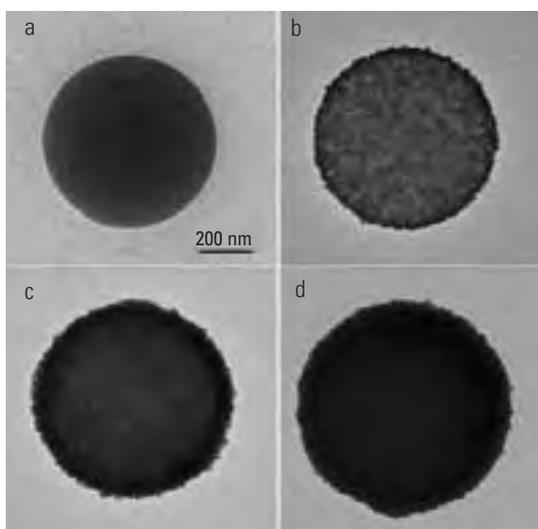


Fig. 2.: TEM micrographs of (a) a two-layer polyelectrolyte-coated polystyrene sphere and identical spheres additionally coated with (b) one, (c) three, and (d) five Au@SiO<sub>2</sub> nanoparticle/polyelectrolyte bilayers.

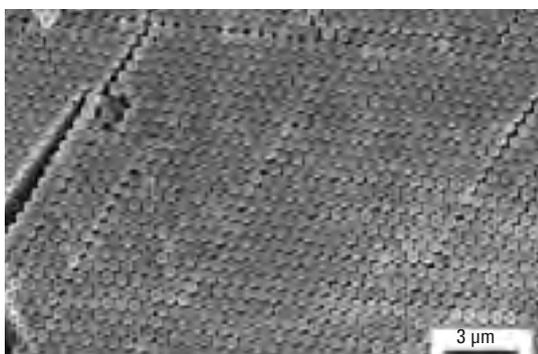


Fig. 3.: SEM image of a colloidal crystal made of polystyrene particles coated with a total of six poly(allylaminehydrochloride)/poly(styrene sulfonate) layers.

### Key Publications:

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

## NON-PLANAR INTERFACES

# Mechanics and Adhesion of Capsules and Strongly Deformable Colloids



### Aims:

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

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

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

### Results:

#### **Measurement of Surface Interactions of Coated Colloids by Colloidal Probe AFM**

(V. Bosio; G. Bogdanovic)

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

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

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

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

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

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

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

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1996: Diploma, Physics

(Universität Konstanz)

Thesis: Measurement of sedimentation velocity of colloids

2000: PhD, Physics

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

2000/2001: Postdoc

(Institute Curie, Paris)

Since 2001: Group Leader

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

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

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

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

A. Fery, G. Bogdanovic, V. Bosio, F. Dubreuil, N. Elsner, J. Heuvingh, M. Nolte  
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### **Key Publications:**

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

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

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

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

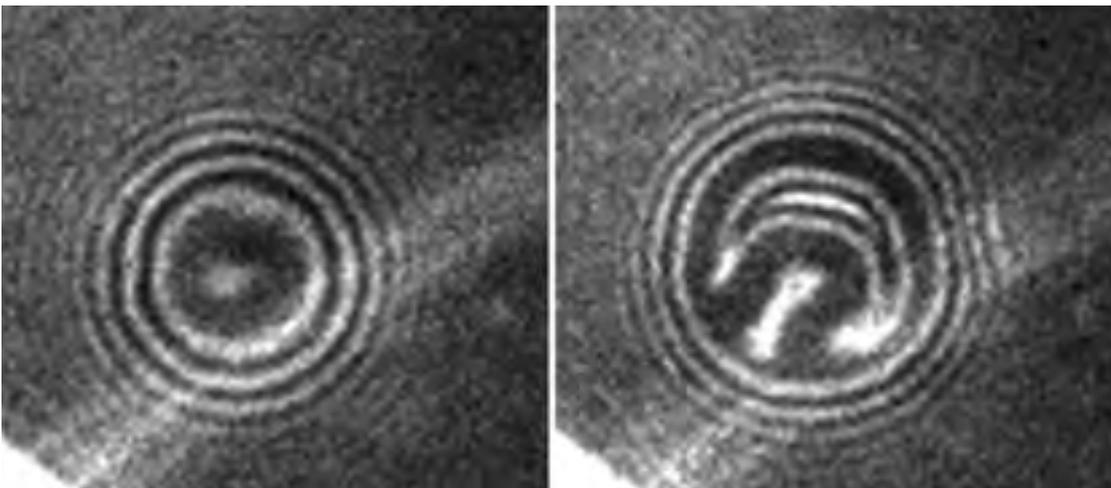


Fig. 1: Interference pattern of a load-free capsule with spherical geometry (left) and the same capsule under load that leads to buckling (right)

## NON-PLANAR INTERFACES

# Modular Materials: From Dynamic to Nano-technological Devices



### Aims:

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

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

### Results:

#### **Metallo-Supramolecular Modules (MEMOs)**

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

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

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

#### **Polyoxometalate Clusters (POMs)**

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

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

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

**Dirk G. Kurth** 06.11.64

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

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

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

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

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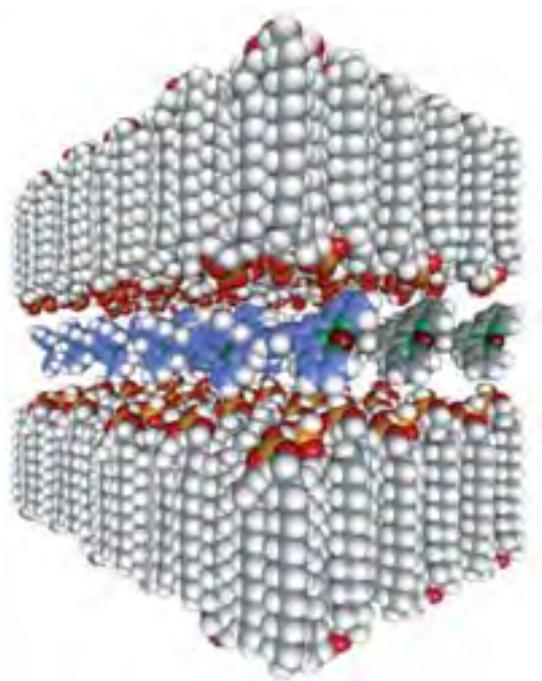


Fig. 1: Representative structure of a PAC mesophase derived by X-ray scattering methods and molecular modeling

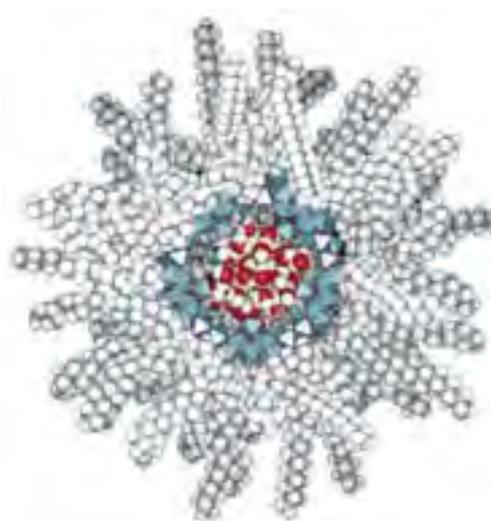


Fig. 2: Molecular modeling study of a surfactant-encapsulated POM cluster. The interior of the Keplerate cluster is filled with water molecules, the exterior is decorated by didodecylammonium molecules.

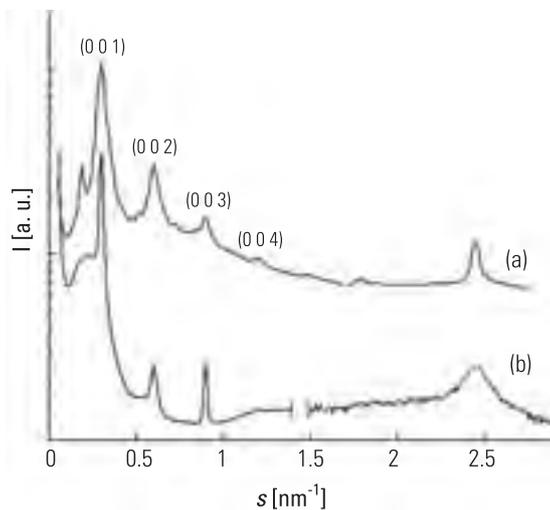


Fig. 3: Calculated (a) and experimental (b) small and wide angle X-ray scattering patterns of PAC. The molecular modeling study shown in Fig. 1 is based on this data.

#### Key Publications:

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

# NON-PLANAR INTERFACES

## Bioinspired Control of Electrical and Optical Properties of Interfaces



### Aims:

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

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

into chemical energy.

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

### Results:

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

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

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

### Future Work:

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

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

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**1971:** Diploma, Physics

(University G $\ddot{o}$ ttingen)

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

**1974:** PhD, Physics

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

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

ESR- und emissionspektroskopische Untersuchungen zwischen 4K und 300 K

**1974-1975:** Postdoc (IBM San Jose)

**1975:** Research Assistant

(University of Ulm)

**1978:** Habilitation, Physics

(University of Ulm)

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

**1978-1981:** Scientific Coworker

(Dornier-System, Friedrichshafen)

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

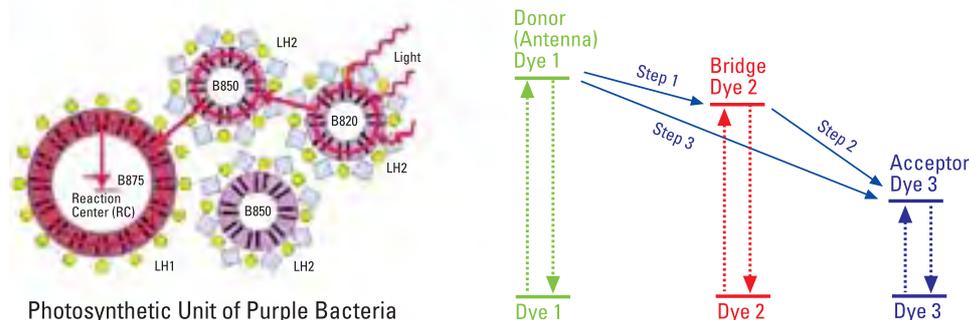
**1987:** Chair C4, Physical Chemistry, (University of Mainz)

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

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

**Since 2001:** Honorary Professor (Zhejiang University, Hangzhou)

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



Photosynthetic Unit of Purple Bacteria

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

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

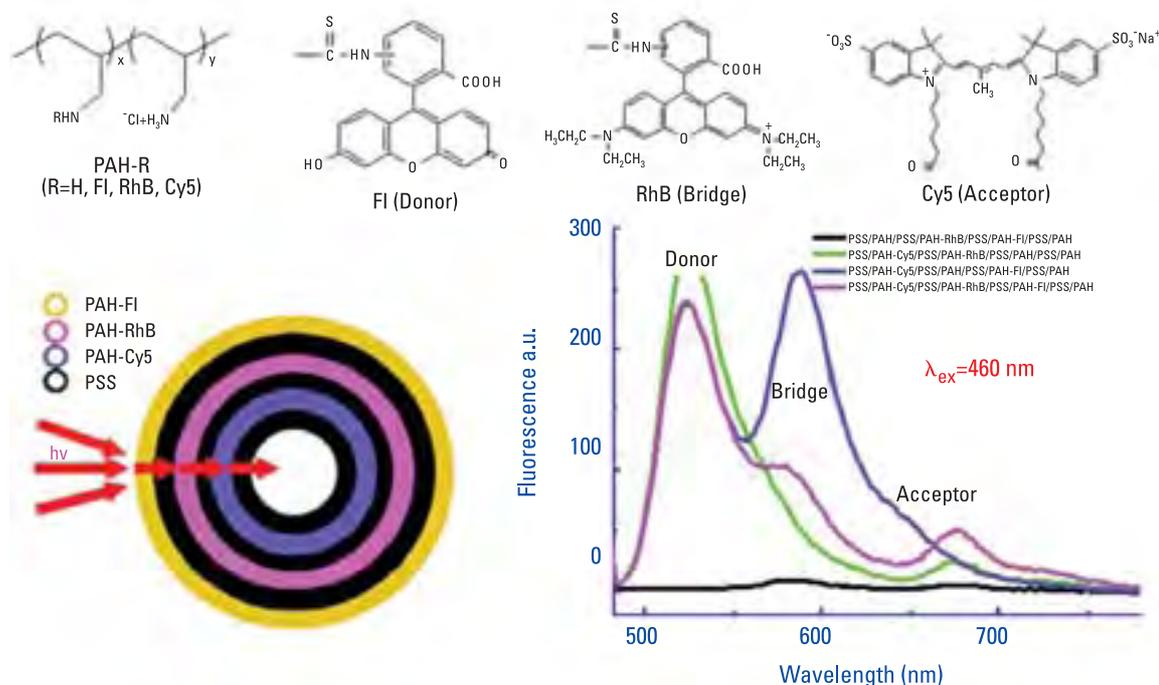


Fig. 2: Energy transfer in chromophore containing capsules schematically (left) and measured via fluorescence emission (right)

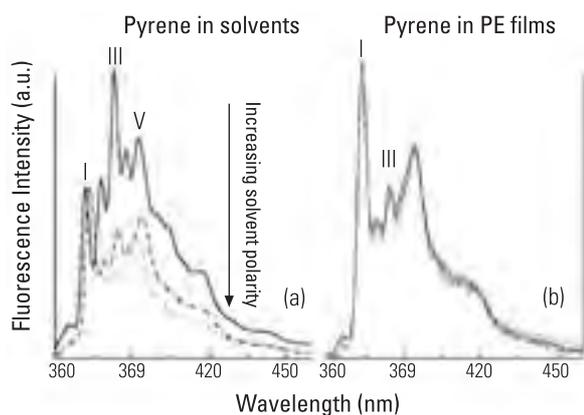


Fig. 3: Fluorescence emission of pyrene in solvents of different polarity (left) and in polyelectrolyte films (right)

### Key Publications:

[1] Tedeschi, C., Caruso, F., Möhwald, H. and Kirstein, S.: Adsorption and Desorption Behavior of an Anionic Pyrene Chromophore in Sequentially Deposited Polyelectrolyte-Dye Thin Films. *J. Am. Chem. Soc.*, 122, 5841-5848 (2000).

[2] Tedeschi, C., Möhwald, H. and Kirstein, S.: Polarity of Layer-by-Layer Deposited Polyelectrolyte Films As Determined by Pyrene Fluorescence. *J. Amer. Chem. Soc.* 123, 954-960 (2001).

[3] Dai, Z. F., Dähne, L., Donath, E., Möhwald, H.: Downhill energy transfer via ordered multi-chromophores in light-harvesting capsules. *J. of Phys. Chem. B*, 106, 11501-11508 (2002).

## Dynamics of Complex Polymer Layers



### Aims:

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

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

### Results:

#### **Lipid Monolayers coupled to Polyelectrolyte Surfaces**

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

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

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

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

#### **Polyelectrolyte Multilayers: Reversible Swelling**

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

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

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

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

#### **Thermoreversible Polymers at Interfaces**

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

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

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

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1990: Diploma, Physics

(Universität Hannover, Germany)

Thesis: Photoionisation cross sections of excited Ba atoms

1994: PhD, Experimental Physics

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Thesis: Photoreorientation of azobenzenes in organic layers

1994-1996: Postdoc (Max Planck

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Berlin-Adlershof, Germany)

1996-1998: Postdoc, Physical Chem-

istry 1 (University of Lund, Sweden)

Since 1998: Group Leader

(Max Planck Institute of Colloids

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

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

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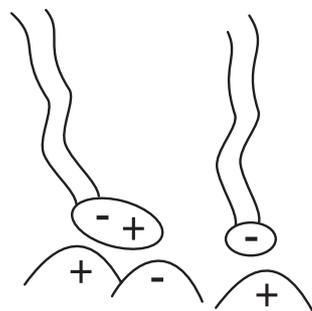


Fig. 1: Model of lipids in monolayers interacting with charged loops of polyelectrolyte multilayers. In air, the zwitterionic lipid shows a stronger interaction than the anionic one.

$\Delta E$ [kJ]	Outer layer: PSS(-)	Outer layer: PAH(+)
DMPC(+/-)	$10.7 \pm 0.7$	$12.1 \pm 1.5$
DOPC(+/-)	$10.6 \pm 1.6$	
DOPA(-)	$8.0 \pm 0.9$	$6.9 \pm 0.5$

Table 1: Activation energies  $\Delta E$  of lipid diffusion in monolayers in contact with polyelectrolyte multilayers

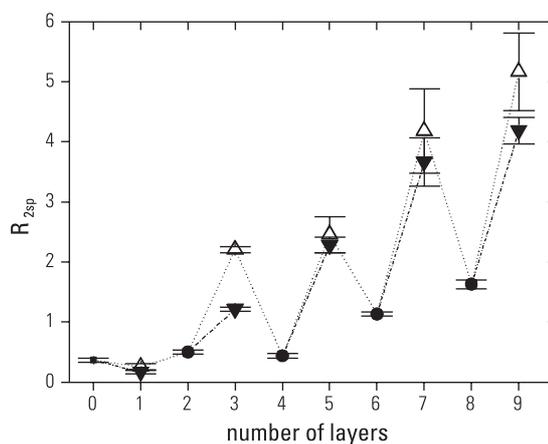


Fig. 2: Specific relaxation rate  $R_{zsp}$  for multilayers of  $(PAH/PSS)_n$  with different polyelectrolytes as last layers:  
 •: PSS (even number of layers),  $\Delta$ : PAH (odd number of layers), and  $\blacktriangledown$ : PDADMAC on top of  $(PAH/PSS)_n$

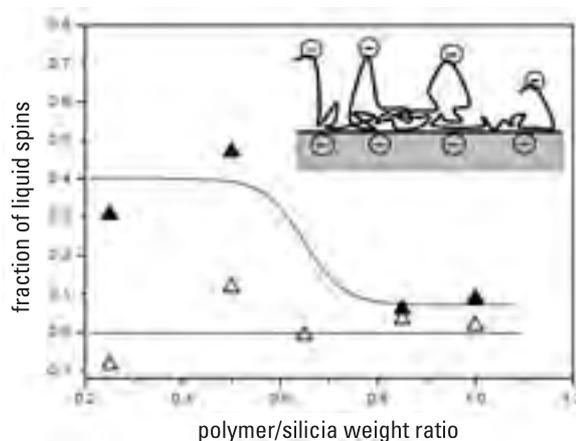


Fig. 3: Fraction of polymer segments in loops and tails, which remain mobile above the phase transition.  $\Delta$ : PNIPAM (uncharged),  $\blacktriangle$ : charged copolymer. Inset: Model of charged segments preventing collapse.

#### Key Publications:

- [1] Wang, L., Schönhoff, M. and Möhwald, H.: Lipids Coupled to Polyelectrolyte Multilayers: Ultraslow Diffusion and the Dynamics of Electrostatic Interactions. *J. Phys. Chem. B* 106, 9135-9142 (2002).
- [2] Schönhoff, M., Larsson, A.; Welzel, P. B. and Kuckling, D.: Thermoreversible Polymers adsorbed to Colloidal Silica: A  $^1H$  NMR and DSC Study of the Phase Transition in Confined Geometry. *J. Phys. Chem. B* 106, 7800-7808 (2002).
- [3] Schwarz, B. and Schönhoff, M.: Surface Potential driven Swelling of Polyelectrolyte Multilayers. *Langmuir* 18(8), 2964-2966 (2002).

## NON-PLANAR INTERFACES

# Multifunctional Polymeric Micro- and Nanosized Capsules



### Aims:

- Nano-engineered ultrathin shell assembly on colloidal particles (study on permeability and release of small molecules)
- Hollow capsules (core decomposition, polymer segregation in multilayers caused by pH, solvent, temperature in order to broaden the possibilities to control the incorporation of macromolecules in capsules, single molecules effects)
- Stimuli-responsive capsules
- Chemical reactions in restricted volumes (precipitation of small organic molecules in capsules, study of their crystalline structures, synthesis of inorganic particles in the capsules)
- Enzymatic reaction in the capsule and artificial cells.

### Results:

#### **Permeability as a Function of Salt:**

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

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

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

#### **Preparation of Thermosensitive Microcapsules:**

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

#### **Nano-Engineered Capsules as Stimuli-Sensors and Microreactors:**

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

#### **Metallized Colloids and Hollow Capsules:**

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

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

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

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**1991:** Diploma, Physics (Lomonosov Moscow State University)

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Thesis: Formation and Investigation of multilayer films containing nucleic acids

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

**1994-1996:** Scientific Researcher (Institute of Crystallography, Russian Academy of Science, Moscow, Russia)

**1997:** Senior Scientist (Institute of Crystallography, Russian Academy of Science, Moscow, Russia)

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

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

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

### Chemical Reaction in Restricted Volumes:

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

The synthesis of inorganic substances exclusively inside polyelectrolyte capsules was performed. Due to the high pH inside the polycation filled capsules the selective synthesis of magnetic  $\text{Fe}_3\text{O}_4$  and non-magnetic hematite  $\text{Fe}_2\text{O}_3$  particles inside the polyelectrolyte capsules filled with polycation was demonstrated. The structure of the resulting particles depends on ratio  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the outer solution. The synthesized  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  core / polyelectrolyte shell composites were characterized by TEM and WAXS techniques. Besides magnetite different ferrites ( $\text{CoFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$ ) were synthesized from corresponding salts exclusively inside polyelectrolyte capsules of 10  $\mu\text{m}$  diameter. Polyelectrolyte capsules with synthesized ferrite (magnetite) particles possess magnetic activity high enough to be easily manipulated in water solution by an external magnetic field. The use of hollow polyelectrolyte capsules as microreactors for spatially restricted inorganic synthesis was shown to be a perspective for further investigation.

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

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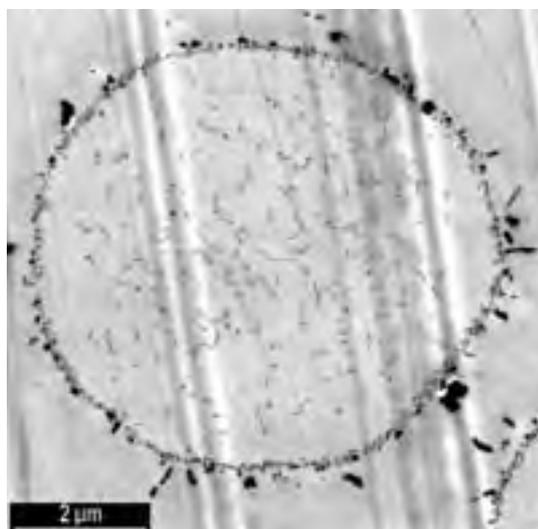


Fig. 1: TEM of thin slice of the silver-filled capsule



Fig. 2: Image demonstrating 20  $\mu\text{m}$  capsules flowing through 10  $\mu\text{m}$  constriction

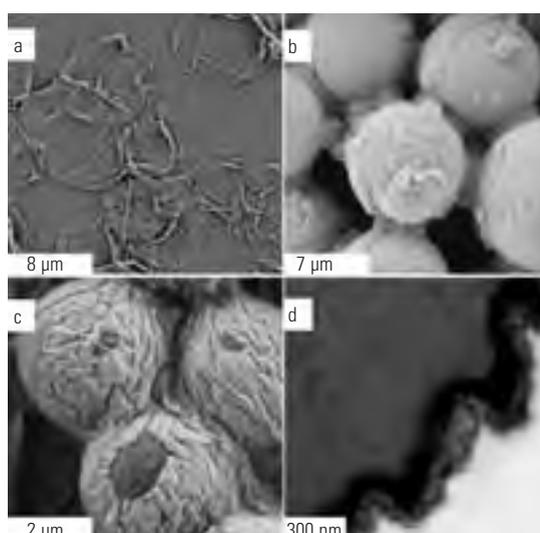


Fig. 3: SEM images of hollow polyelectrolyte capsules (a) and polyelectrolyte capsules filled with  $\text{Fe}_3\text{O}_4$  (b) and  $\text{YF}_3$  (c). (d) – TEM image of an ultramicrotomed polyelectrolyte capsule filled with  $\text{Fe}_3\text{O}_4$

### Key Publications:

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

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



### Summary:

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

### Aims:

The focus is on the following topics/questions:

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

### Results:

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

### Excess Coverage

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

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

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

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

### Submonolayer Coverage

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

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**1982:** Diploma, Physics

(Ludwig-Maximilians-Universität Würzburg) Thesis: Lichtinduzierte Diffusion in Gasen

**1986:** PhD, Physics

(Technische Universität München) Thesis: Protein/Lipid-Wechselwirkungen von Photosynthetischen Reaktionszentren und Cytochrom C mit Modellmembranen

**1986-1988:** Postdoc (AT&T Bell Laboratories in Princeton, NJ)

**1988-1994:** Group Leader

(Mainz University)

**Since 1994:** Group Leader

(Max Planck Institute of Colloid and Interfaces, Golm)

**1996:** Habilitation (Mainz University)

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

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

### Future Perspectives:

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

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

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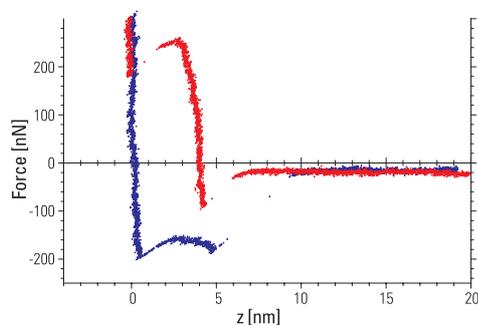


Fig. 2: Force spectroscopy of a solid alkane monolayer on a  $\text{SiO}_2$ -surface. The red curve is obtained on approach, the blue one on receding of the tip to/from the surface.

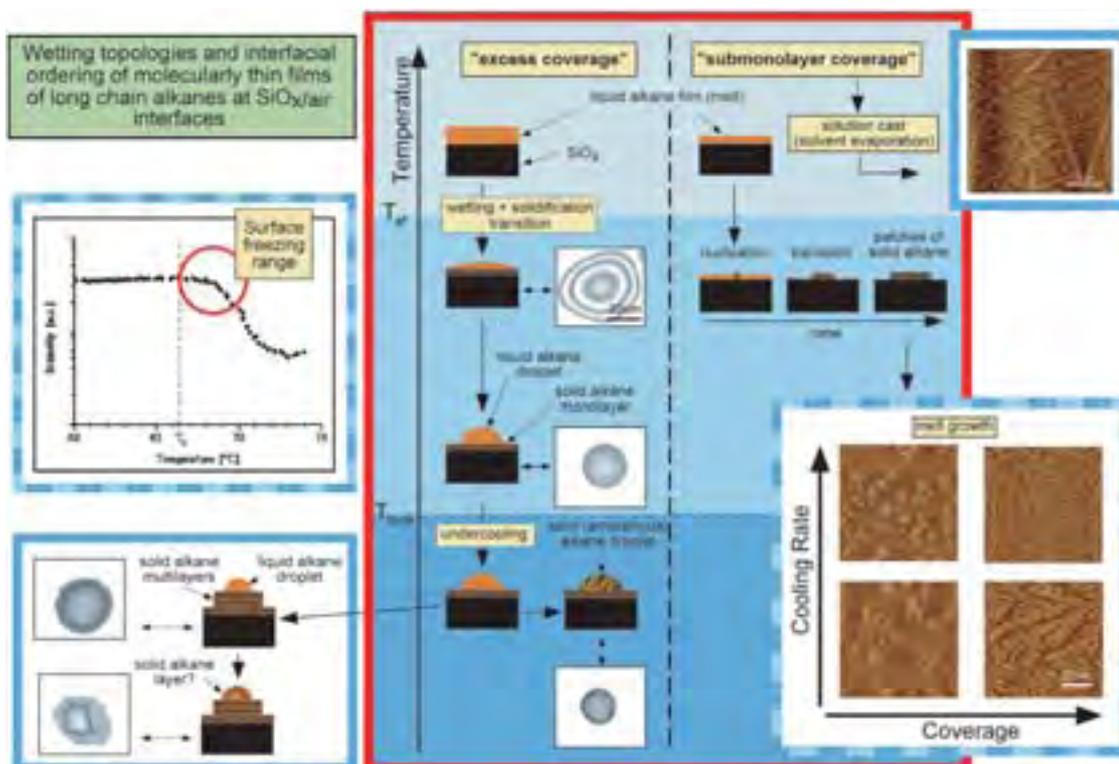


Fig. 1: Overview over the various interfacial ordering, nucleation and wetting phenomena of long chain alkanes at solid/air interfaces

### Key Publications:

- [1] Schollmeyer, H., Ocko, B. and Riegler, H.: Surface Freezing of Triacotane at  $\text{SiO}_2$ /Air Interfaces: Submonolayer Coverage. *Langmuir* 18, 4351-4355 (2002).
- [2] Riegler, H. and Essler, F.: Polyelectrolytes. 2: Intrinsic or Extrinsic Charge Compensation? Quantitative Charge Analysis on PAH/PSS Multilayers. *Langmuir* 18, 6694-6698 (2002).
- [3] Schollmeyer, H., Struth, B. and Riegler, H.: Long chain n-alkanes at  $\text{SiO}_2$ /air-interfaces: Molecular ordering, annealing, and surface freezing of triacotane in the case of excess and submonolayer coverage. *Langmuir*, in press.

## Assembly of Complex and Biomimetic Materials



### Complex Molecular Assembly in Aqueous Solution

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

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

### Enzymatic Reaction via Molecular Recognition

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

**Results:** Optical microscopy is used to follow the enzyme influence on molecular arrangement, catalytic activity and impact of inhibitor. It has been verified that the selected inhibitor has inhibited the cleavage of the L-DPPC monolayer by PLA<sub>2</sub>. The enzymatic hydrolysis reaction has been dynamically observed with Brewster angle microscopy. Addition of an indole derivative as inhibitor postponed the formation of "C" or "O" types of domains, and correspondingly delayed the cleavage of L-DPPC. Our experimental results provide a possibility for a direct proof of an inhibitor capacity.

### Mixed Lipid/Protein Complexes at Interfaces

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

### Biointerfacing Microcapsules

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

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

Leaving such vesicles in phospholipase A<sub>2</sub> solution we observed the hydrolysis reaction on the surface of the lipid/polymer vesicles and permeability change before and after reaction by confocal laser scanning microscopy (CLSM). Thus a capsule with permeability adjustable by enzymatic hydrolysis of the lipid layers adsorbed on the surface of a multilayer polyelectrolyte capsule was constructed.

### Biogenic Capsules

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

J. B. Li, S. F. Ai, Z. H. An, G. C. Cui, L. Q. Ge, Q. He, G. Lu, C. Tao, X. L. Wang, X. H. Zhai, H. J. Zhang, Y. Zhang, S. P. Zheng, H. F. Zhu; Collaborated with Max Planck Institute of Colloids and Interfaces: G. Brezesinski, H. Möhwald, H. Motschmann  
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**Junbai Li** 01.12.1964

**1989:** Diploma, Chemistry

(Jilin University, China)

Thesis: Photon Correlation Spectroscopy Investigation of Ultrafine Polymer Particles

**1992:** PhD, Chemistry

(Jilin University, Mainz University)

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

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

**1993-1996:** Postdoc

(Max Planck Institute of Colloids and Interfaces, Golm)

**1996-1999:** Full Professor

(International Joint Lab, Institute of Photographic Chemistry, Chinese Academy of Sciences)

**Since 1999:** Full Professor

(International Joint Lab, Max Planck Institute of Colloids and Interfaces and Institute of Chemistry, Chinese Academy of Sciences)

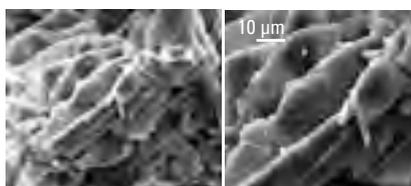


Fig. 1: SEM images of the lamellar CdS crystals

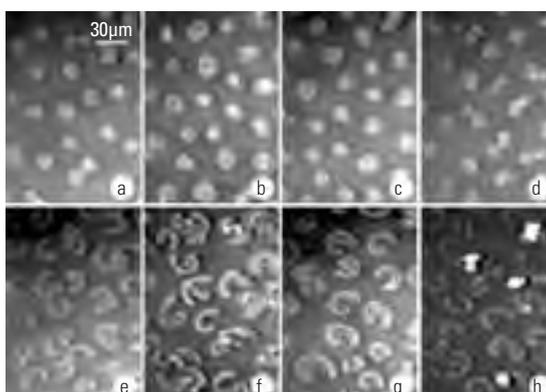


Fig. 2: BAM images of a mixed monolayer of inhibitor/L-DPPC (30:1) after injection of PLA<sub>2</sub>. The images were taken 0 (a), 6 (b), 55 (c), 60 (d), 67 (e), 74 (f), 77 (g), 78 (h) minutes after starting the hydrolysis reaction at  $\pi_0 = 12 \text{ mNm}^{-1}$ .

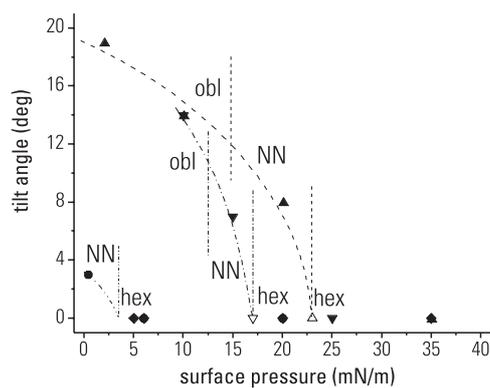


Fig. 3: Phase diagram (tilt angle  $t$  as a function of lateral pressure  $\pi$ ) of DPPA monolayers on pure water (▲), on buffer (▼), on HSA (essentially fatty acid free) solution (●) and on HSA (glycated) solution (◆). Open symbols represent extrapolated values. obl (oblique with intermediate tilt),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

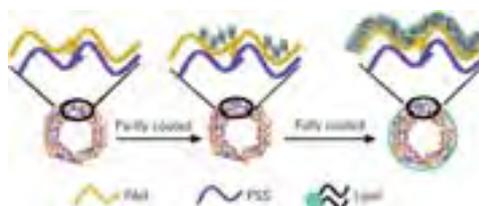


Fig. 4: Scheme for the surface of polyelectrolyte capsules, partly lipid covered capsules and fully lipid covered capsules.

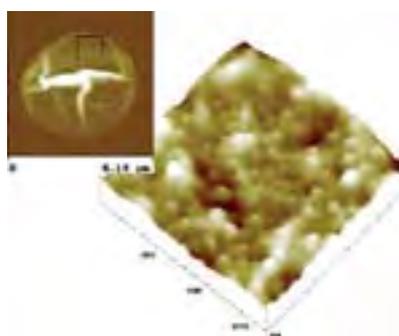


Fig. 5: SFM image of multilayer polyelectrolyte capsules fully covered by pure DMPA in a dried state and a selected dried (PSS/PAH)<sub>2</sub>/DMPA surface morphology.

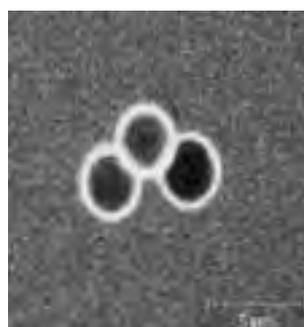


Fig. 6: CLSM image of a partly PLA<sub>2</sub> catalyzed capsule. The dye molecules can penetrate into the capsule, but the dye concentration inside is lower than outside.



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

#### Key Publications:

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

# Research Group Nanotechnology for Life Science

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



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

have worked together on such a pilot project.

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

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

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

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

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

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

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

### **Polymers, Proteins and Protein Stability**

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

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

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

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

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

**Andreas F. Thünemann** 16.08.1964

**1991:** Diploma, Chemistry

(Philipps Universität Marburg)

Thesis: Cyclization of Polyacrylonitrile

**1995:** PhD, Chemistry

(Philipps University Marburg)

Thesis: Strukturumwandlungen

und Bildung von Mikrophasen in

Homopolymeren, Copolymeren und

Metallcarbonylen des Acrylnitrils

**2000:** Postdoc, Research Scientist

(Heinrich-Heine-Universität Düsseldorf)

**1995-2001:** Group Leader

(Max Planck Institute of Colloids

and Interfaces, Golm)

**2001:** Habilitation, Physical Chemistry

(Potsdam University)

Thesis: Self-Assembly, Ordered

Nanostructures and Functionality of

Polyelectrolyte-Amphiphile Complexes

**Since 2002:** Group Leader

(Fraunhofer-Institut für Angewandte

Polymerforschung, Golm)

### Polymer-Lipid Nanoparticles as Drug Carrier Systems

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

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

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

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

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### Key Publications:

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

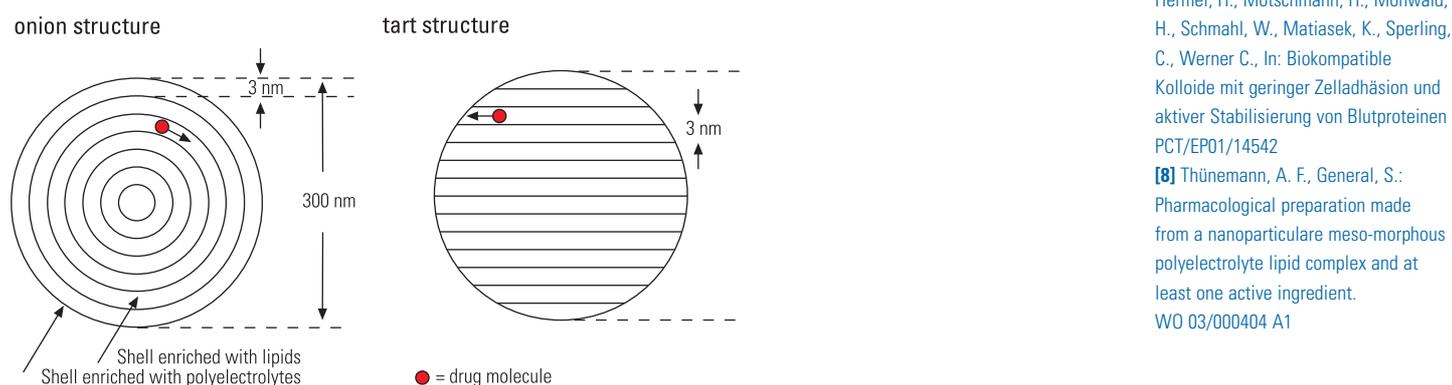
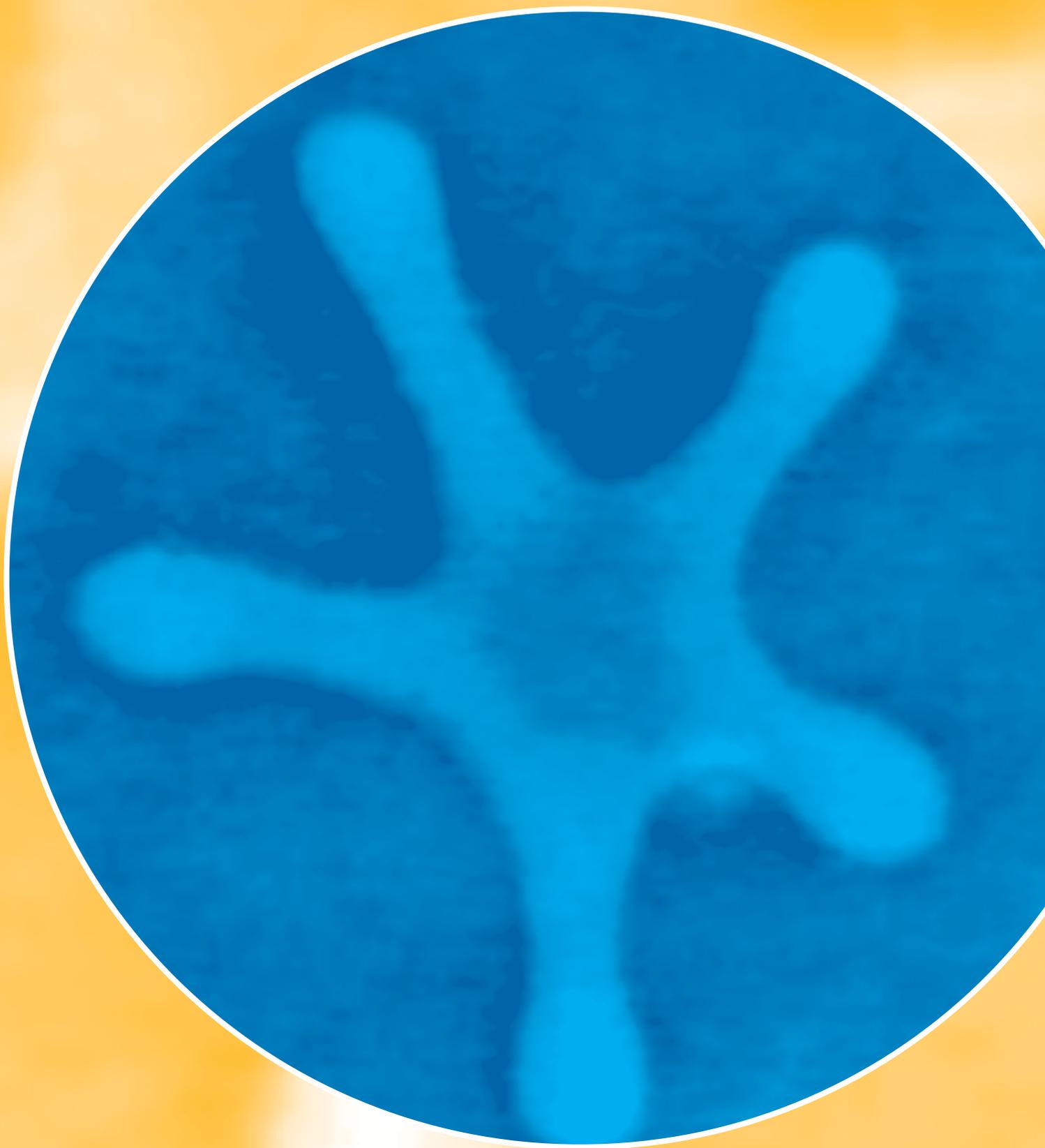


Fig. 1: A schematic representation of a drug carrier system consisting of polyelectrolyte-lipid complexes with a typical size of 300 nm. The stability of the nanoparticles is achieved by the polymers. The inner structure of the particle with a characteristic length of 3 nm is given by the lipids. A lipophilic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

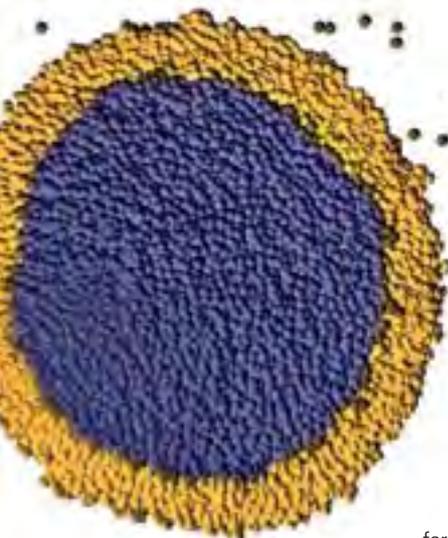


# THEORY

THEORY



# Research in the Theory Department



Research in the theory department is focused on generic aspects of colloids and interfaces such as structure formation, polymorphism, morphological transitions, entropic forces, and active behavior. In many cases, our theoretical models are inspired by the colloidal architecture of biomatter, which corresponds to the basic levels of life and which includes assemblies and super-assemblies of biomolecules as previously described on page 13.

The conceptual framework for the understanding of these systems and their cooperative behavior is provided by statistical physics which includes thermodynamics, statistical mechanics, and stochastic processes.

Most associates of the theory department perform theoretical work using the analytical and numerical methods of theoretical physics. In addition, some experimental work is carried out in our membrane lab, using optical microscopy, micropipettes, and isothermal titration calorimetry, and in the DESY lab of the MPI.

The theory department is divided into several groups. During 2001 and 2002, seven groups were primarily funded by the Max Planck Society:

- Christian Seidel (theory, polymers and polyelectrolytes)
- Roland Netz, now at the University of Munich (theory, polyelectrolytes and charged systems)
- Jan Kierfeld (theory, polymers and filaments)
- Rumiana Dimova (experiment, membranes and vesicles)
- Julian Shillcock (theory, supramolecular modeling)
- Angelo Valleriani (theory, evolution), now program coordinator of the IMPRS on „Biomimetic Systems“
- Thomas Gruhn (theory, membranes and vesicles)
- Thomas Weikl (theory, proteins and membranes)

In addition, three groups were primarily funded externally:

- Hans-Günther Döbereiner, now at Columbia University (experiment, membranes and vesicles), funded by Heisenberg fellowship of DFG
- Willi Fenzl at DESY lab (experiment, X-ray scattering), funded by BMBF
- Ulrich Schwarz (theory, membranes and cells), funded by Emmy Noether fellowship of DFG

## Structural Hierarchy and Theoretical Concepts

The structural hierarchy of colloids and interfaces implies a hierarchy of theoretical concepts. Indeed, for each level of this hierarchy, one needs to develop a separate description which identifies the useful concepts and the relevant parameters for that level. This is a challenge which is not always appreciated.

In fact, one often hears statements of the sort that, in principle, any system consisting of many atoms is governed by a 'huge' Schrödinger equation which describes the quantum-mechanical motion of the atomic nuclei and of the electrons. However, even if we were able to obtain a complete solution for the quantum-mechanical motion of all the nuclei and electrons, we would not be able to understand the meaning of this solution. Indeed, such a complete solution would represent an enormous amount of mostly useless information. Therefore, even if we had no technical problems with such a solution, we would still have to identify the various structural levels and the concepts and parameters which are appropriate for those levels.

## Top-Down: Thermodynamics of Interfaces and Membranes

Thermodynamics represents a very robust theoretical framework which provides a top-down route into the colloidal regime and which depends on a relatively small number of parameters. Using this framework in the micrometer regime, interfaces can be characterized by their Laplace pressure, interfacial tension, and contact angles. This framework is also appropriate to describe wetting morphologies on structured surfaces as we have shown during the last couple of years.

There are two simple extensions of this framework: (i) In the nanometer regime, the wetting morphologies are also affected by the line tension of the contact line which one must include as an additional parameter in the thermodynamic description; and (ii) Fluid membranes such as lipid bilayers can be understood using the same theoretical framework if one includes the bending energies with depend on membrane curvature. In the simplest case, this involves only one additional parameter, the bending rigidity of the membrane.

### **Bottom-Up: Statistical Mechanics of Supramolecular Structures**

The bottom-up approach starts from coarse-grained models for molecules or monomers. Linear chains of such monomers provide relatively simple models for homo- and copolymers. Membranes can be modeled on the nanometer scale using simplified amphiphilic molecules which assemble into bilayers. On larger scales, they behave as flexible elastic sheets which can be characterized by their bending rigidity. In both cases, one can include several components in order to mimic the behavior of multicomponent biomembranes.

These models are studied using a wide range of theoretical methods: variational methods to determine the most probable state; scaling arguments and self-consistent theories; transfer matrix methods for 1-dimensional polymers and filaments; field-theoretic methods; computer simulations based on Monte Carlo, Molecular Dynamics, and Dissipative Particle Dynamics.

Using the latter method it is now possible to simulate vesicles with a diameter of about 30 nanometers.

### **Brownian Motion and Entropic Forces**

At finite temperatures, all colloidal particles undergo Brownian motion as a result of thermally-excited collisions with the solvent molecules. Likewise, flexible colloids such as membranes and filaments undergo thermally-excited shape fluctuations which represent the Brownian motion of many coupled degrees of freedom. These shape fluctuations lead to entropically induced forces which compete with the attractive van der Waals or electrostatic forces between different colloidal structures.

The competition between molecular interactions and entropic forces has been recently studied for the adhesion of vesicles, for the sticker-mediated adhesion of membranes, and for the adsorption and bundling of semiflexible polymers or filaments.

In all cases, one finds that the entropic contributions renormalize the molecular interactions and lead to structural transitions within these systems.

In the case of membrane adhesion mediated by stickers and repellers, sticker-rich domains appear in the contact area and form certain patterns with a characteristic time evolution. A similar pattern formation process has been recently observed for the immunological synapse between cells of the immune system.

### **Active Behavior of Colloids**

Biological cells are very active: They can easily deform their shape, move, crawl, and grab onto underlying surfaces. Likewise, the intercellular arrangement of vesicles and organelles is constantly reshuffled and one observes heavy traffic of these colloidal objects. One extreme case is cell division (mitosis) which leads to the spectacular segregation of chromosomes. All of these processes are based on the cooperative behavior of active nanostructures such as filament monomers and molecular motors.

We have recently studied several aspects of this active behavior theoretically: ratchet models for the force generation by motors; lattice models for the transport by molecular motors in open and closed compartment; motor traffic involving the collective transport of many cargo particles; the formation of traffic jams arising from the strong adsorption of the motors onto the filaments; active phase transitions induced by changes in the boundary conditions as the motors enter and leave the compartments; active pattern formation in closed compartments.

Current projects on active biomimetic systems include: active force generation by polymerization; active noise of filaments and membranes; active assembly and disassembly of filaments and motors.

For more information, see the following, more detailed reports of some of our projects and the web sites:

<http://www.mpikg-golm.mpg.de/th/>

<http://www.mpikg-golm.mpg.de/lipowsky>

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# Wetting Phenomena at Structured Surfaces



Many experimental methods have been developed by which one can prepare chemically structured substrates with patterns of lyophilic (or liquid attracting) and lyophobic (or liquid repelling) surface domains. The linear size of the surface domains can be varied over a wide range of length scales from the millimeter down to the nanometer regime. We have recently discovered that such chemically structured surfaces lead to morphological wetting transitions at which the wetting layer changes its shape or morphology in a characteristic and typically abrupt manner [1, 2].

From the theoretical point of view, these wetting morphologies correspond to bifurcations of mean curvature surfaces which are pinned along their edges by the surface domain boundaries.

Presumably the simplest surface domain pattern consists of a single lyophilic stripe on a lyophobic surface. The stripe has width  $L_1$  and has a length which is large compared to  $L_1$ . The lyophilic stripe and the lyophobic substrate are characterized by different contact angles  $\theta_\gamma$  and  $\theta_\delta$  respectively. Now, imagine that we start to deposit liquid  $\beta$  on the lyophilic stripe.

## 'Painting' Striped Surface Domains

The liquid will first form a small droplet which grows until its contact line touches the boundary of the surface domain. What happens as one continues to add liquid and the droplet continues to grow?

It turns out that the subsequent evolution of the wetting layer morphology depends in a very sensitive way on the contact angle  $\theta_\gamma$  of the lyophilic stripe. [3] Indeed, this contact angle exhibits a threshold value  $\theta_{ch}(\infty)$  which separates two different wetting regimes. These two regimes are characterized by qualitatively different behavior as the volume of the deposited liquid is further increased. If the stripe has contact angle  $\theta_\gamma < \theta_{ch}(\infty)$ , the wetting layer forms a channel which becomes longer and longer as one deposits more and more liquid. For  $\theta_\gamma > \theta_{ch}(\infty)$ , on the other hand, such a long channel cannot be attained but only a short one which gradually transforms into a localized droplet. In other words, it is easy to 'paint' long  $\gamma$  stripes provided  $\theta_\gamma < \theta_{ch}(\infty)$  but it is impossible to do so for  $\theta_\gamma > \theta_{ch}(\infty)$ . The corresponding bifurcation diagram is shown in Fig. 1.

## Liquid Bridges in Structured Pores

Another geometry which can be realized experimentally are slit pores and slabs bounded by structured surfaces. The simplest pattern of surface domains consists of a single pair of opposing lyophilic stripes.

If the striped surface domains are relatively long, one may often ignore effects arising from their ends. In such a situation, the wetting morphologies are translationally invariant parallel to the stripes and are completely determined by their cross-section. However, if one takes the finite length of the surface stripes into account, one often finds bridges which are localized in space and, thus, are far from any translationally invariant state; one example is shown in Fig. 2. [4]

## Line Tension Effects

As one studies smaller and smaller systems, the wetting morphologies will also be affected by the line tension, i.e., by the free energy of the contact line. The contact angle along this line satisfies a generalized Young equation which we have derived for the most general case of topologically rough and/or chemically patterned substrates. [5]

Our equation for the contact angle contains a new term which has been recently confirmed experimentally by the group of Stefan Herminghaus, see Langmuir 18, 9771 (2002).

## Nucleation and Growth

Wetting is intimately related to surface nucleation. Thus, the nucleation at chemically structured surfaces exhibits new and interesting features which reflect the different droplet patterns which can be formed on these surfaces. One particularly interesting aspect is that these nucleation processes can lead to metastable wetting morphologies.

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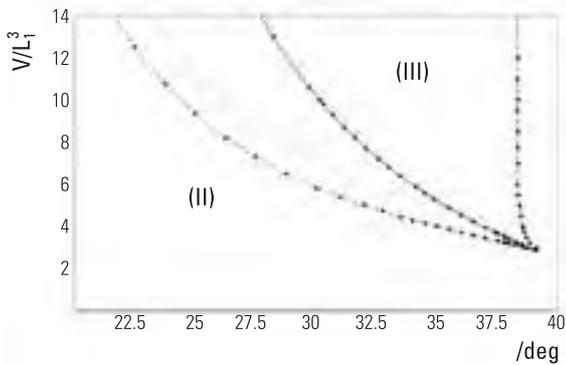


Fig. 1: Bifurcation diagram for liquid morphologies on one lyophilic stripe. The two parameters  $\theta_\gamma$  and  $V/L^3$  are the contact angle on the lyophilic stripe and the reduced volume of the liquid phase, respectively. The full line represents the line of discontinuous transitions from channel states (II) to bulge states (III). The dashed lines represent the instability lines for these two morphologies. The dotted lines are analytical estimates.

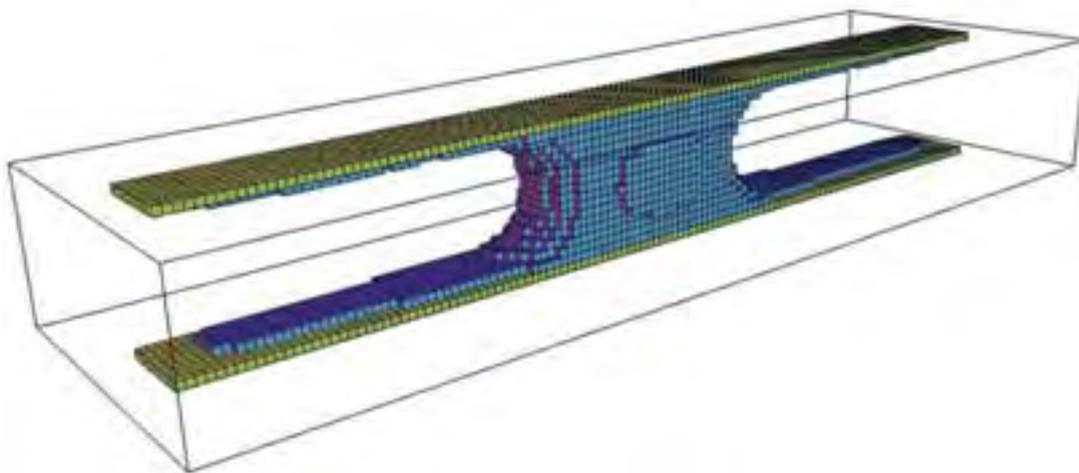


Fig. 2: Localized bridge within a slit pore or slab bounded by two structured surfaces with a lyophilic  $\gamma$  stripe as obtained from lattice gas simulations.

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# Wetting Transitions of Hydrocarbons on Water



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The wetting behavior of hydrocarbons on water is exceptional both from an experimental and theoretical point of view. Wetting transitions of pentane, hexane and heptane on water have been studied by the group of D. Bonn using ellipsometry as an experimental technique [1-3]. After a discontinuous jump from a microscopically thin film to a film with about 10 nm thickness, a continuous increase of the film thickness with increasing temperature up to 100 nm for pentane and 30 nm for hexane has been observed. The authors of Ref. [1-3] conclude that this continuous increase is indicative for a continuous wetting transition. This conclusion is mainly based on a calculation in which the nonretarded van der Waals interaction is superposed with a next-to-leading term  $b(T)d^{-3}$ . Although this procedure has been used in a lot of theoretical papers, it is not recommended, because especially for hydrocarbons on water, the film thickness is determined by the interplay of the nonretarded static and the retarded dispersion interaction, which can even have a different sign.

Recently the dielectric function of water has been experimentally measured over a large energy range using inelastic x-ray scattering experiments [4, 5]. Using these data the dispersion part of the van der Waals interaction of a pentane film on water from the triple point up to the critical point of pentane has been calculated.

In Fig. 1 the result for a temperature slightly below the wetting transition is shown together with the static part of the van der Waals interaction. For a small film thickness the dispersion part is already positive below the wetting transition. For an intermediate film thickness above about 5 nm, the dispersion part becomes negative. Extrapolating the nonretarded dispersion interaction to film thicknesses beyond about 1 nm is therefore not meaningful. For a large film thickness beyond 100 nm the repulsive static van der Waals interaction dominates. The results of our calculation show that a wetting transition of hydrocarbons on water cannot be continuous because both the dispersion and the static part are repulsive at large film thickness already below the wetting transition. The wetting transitions of alkanes on water belong to a scenario, where the film thickness increases up to large values but finally jumps discontinuously to infinity. It is also observed that the temperature of the wetting transition is higher than the temperature, where the nonretarded van der Waals interaction changes its sign.

If the wetting transition of hydrocarbons on water would be in fact continuous, one has to look for a mechanism to cancel the static van der Waals interaction. Electrolytes dissolved in the liquid film could screen the static van der Waals interaction, but their solubility is very low in alkanes. But even if a fluctuation induced attraction like the acoustical casimir effect would balance the static interaction, the dispersion part alone is repulsive at large film thickness due to the very different dielectric susceptibilities of water and alkanes for infrared frequencies.

The temperature dependence of the measured film thickness of pentane and hexane on water does not agree well with a power law with an exponent of -1 as expected from a superposition of the nonretarded van der Waals interaction with a term  $b(T)d^{-3}$ . For the case of hexane on water containing 1.5 M NaCl this has been already mentioned in [2], but there is no reason why pentane should show an exponent -1 and hexane not. For pentane on water the Log-Log plot presented in Fig. 1 of [1] is not convincing. Moreover, if one combines data, which are presented in [2] with those of [1], the deviation from a power law becomes better visible. It is now clearly seen that the film thickness of pentane and hexane on water is increasing very slowly over a temperature range of about 10-20 K after a discontinuous pretransition. Then, a steep increase of the film thickness occurs. DLP theory predicts film thicknesses which are not far from the observed ones, but they fail to predict the observed temperature dependence. This indicates that a quantitative prediction of the temperature dependent film thickness of alkanes on water has to go beyond the sharp kink approximation. In turn this would also affect the evaluation of the ellipsometric data.

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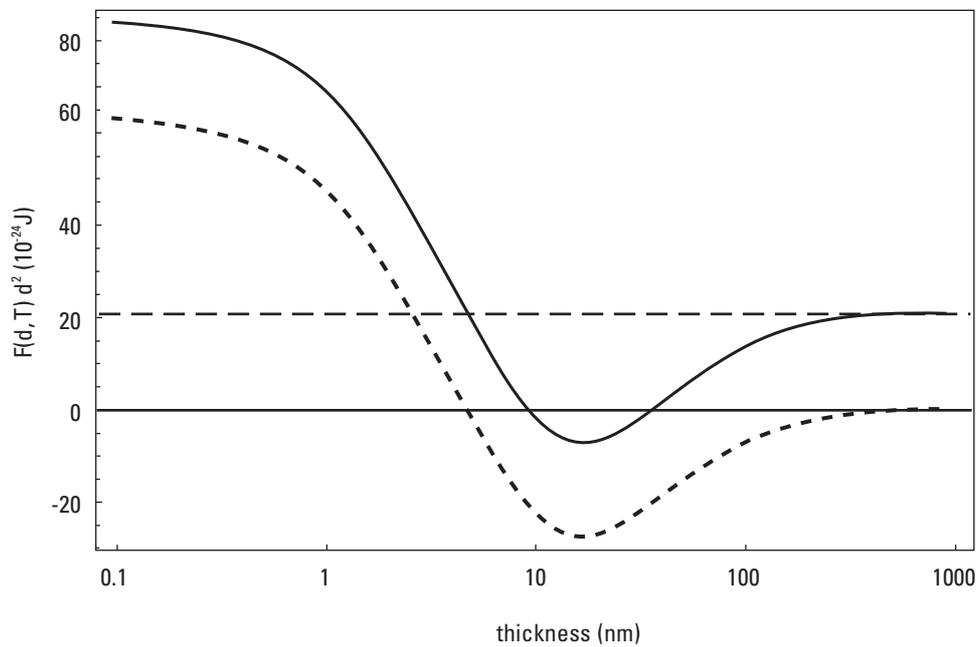


Fig. 1: Van der Waals interaction of a pentane film on water close to the wetting transition, multiplied with the square of the film thickness. The dashed line represents the static part, the dotted line the dispersion part and the full line the sum of both parts.

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# Mesososcopic Simulations of Biomimetic Membranes



Lipid bilayer membranes surround living cells, protecting their interior from the outside world. They are much more than a static structural component, however, in that their composition and dynamics influence membrane-bound proteins, and contribute to the remarkable material properties of cells such as red blood cells. Bilayer membranes also surround artificial vesicles, and have been constructed out of

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non-biological amphiphiles (zu Putlitz et al., 2000), and diblock copolymers (Discher et al., 2000). These membranes continually undulate owing to the thermal motion of their constituent lipids. Thermal forces combine with specific molecular forces to create complex, dynamic, multi-component systems. Dynamic processes taking place within a membrane can involve cooperative changes over distances large compared to the molecular size, and occur on time-scales much longer than molecular vibrational periods.

Biomimetic membranes surround vesicles and artificial cells, and have many properties in common with natural membranes. Because they usually contain only one or a few types of molecule, they are much simpler to investigate experimentally, and so are used as model systems. As a result of their experimental importance, there is a great demand for a theoretical understanding of the dependence of membrane properties on their composition and the architecture of their constituent molecules. The rapid increases in the speed and memory capacity of computing technology in the last decade has permitted the development of new techniques for investigating the material properties of biomimetic membranes, of which we are using two: Coarse-grained Molecular Dynamics (MD) and Dissipative Particle Dynamics (DPD) simulations.

Traditional MD simulations are limited to a few thousand atoms even with the fastest current computers. This limitation arises from the hard-core interaction at the heart of the interatomic potentials used to represent the interactions between molecules. This necessitates a small time-step, to avoid huge forces developing when two atoms approach closely, which limits both the spatial and temporal extent of the simulation. Coarse-grained Molecular Dynamics keeps the potentials of the classical MD but treats the particles in the simulation as groups of atoms instead of individual atoms. This leads to an increase in the spatial size of system that can be simulated.

Using this technique, we have measured the shape fluctuations of a patch of lipid bilayer containing 1152 lipid molecules. The membranes exhibit long wavelength fluctuations that significantly affect their bending stiffness. Time-dependent phenomena, such as the lipid diffusion coefficient, of two-component membranes have also been studied and recently submitted for publication (Imparato, Shillcock and Lipowsky, 2002). However, these simulations are still limited in space and time by the potentials.

Moving further into the mesoscopic realm, DPD simulations are based on the premise that at length scales much larger than the atomic, which encompasses many cellular

processes of interest, such as cell adhesion, rupture and fusion, the motion of individual atoms is irrelevant. Averaging over these small-scale motions loses detailed information but greatly increases the length and time scales accessible to the simulations. We have used DPD to investigate the material properties of lipid bilayer patches and complete vesicles, comparing the results with traditional Molecular Dynamics simulations where possible. The elastic properties of a bilayer patch containing over 3000 lipids agree well with coarse-grained MD as a recent publication of our group shows (Shillcock and Lipowsky, 2002). Having thus validated the technique, we are now investigating the process of membrane fusion.

Fusion of lipid bilayers is a fundamental process in many kinds of cell, ranging from synaptic vesicle fusion in neurons to viral penetration of host cells. Fusion events typically involve proteins, although the molecular details of their action remains unclear.

Fusion of artificial vesicles has been promoted, in the absence of proteins, by several means, such as distributing divalent anions between the two fusing vesicles; employing exotic triple-chained amphiphiles in the fusing vesicles; and inducing a Marangoni flow of lipids away from the fusion zone as a consequence of the dehydrating effects of non-adsorbing polymers close to the fusing bilayers (Safran et al., 2001). Cells and vesicles do not routinely fuse with one another, showing that the lamella phase of lipid bilayers is normally stable against such processes; and yet the lamella phase can be driven along a pathway that, locally, promotes mixing of the bilayers and the formation of a pore connecting the interior volumes. The detailed structural rearrangements of lipid molecules that occur on the path to fusion are still a mystery. We are using DPD simulations to study the fusion of a vesicle to a planar bilayer induced by condensing a patch of lipids far from the fusion zone in a simutational analog of the Marangoni effect mentioned above.

When a relaxed vesicle containing approximately 6400 lipids is placed near a tense lipid bilayer, which contains 3600 lipids, its shape fluctuations cause it to encounter the proximal bilayer leaflet.

Once a few lipids bridge the water gap between the two membranes, we externally induce a surface tension gradient in the planar membrane's proximal leaflet resulting in a flow of lipids from the vesicle into the bilayer. This leads to the formation of a pore in the tense bilayer and fusion of the vesicle (**Fig. 1**). We are currently investigating the precise conditions under which fusion occurs, but note that the simulated fusion sequence agrees with the hypotheses underlying current models of cell fusion (Jahn and Grubmueller, 2002). The next stage in this work is to model the proteins that regulate fusion in living cells, and to explore further the complex interplay of forces that dominates the mesoscopic world of biomimetic systems.

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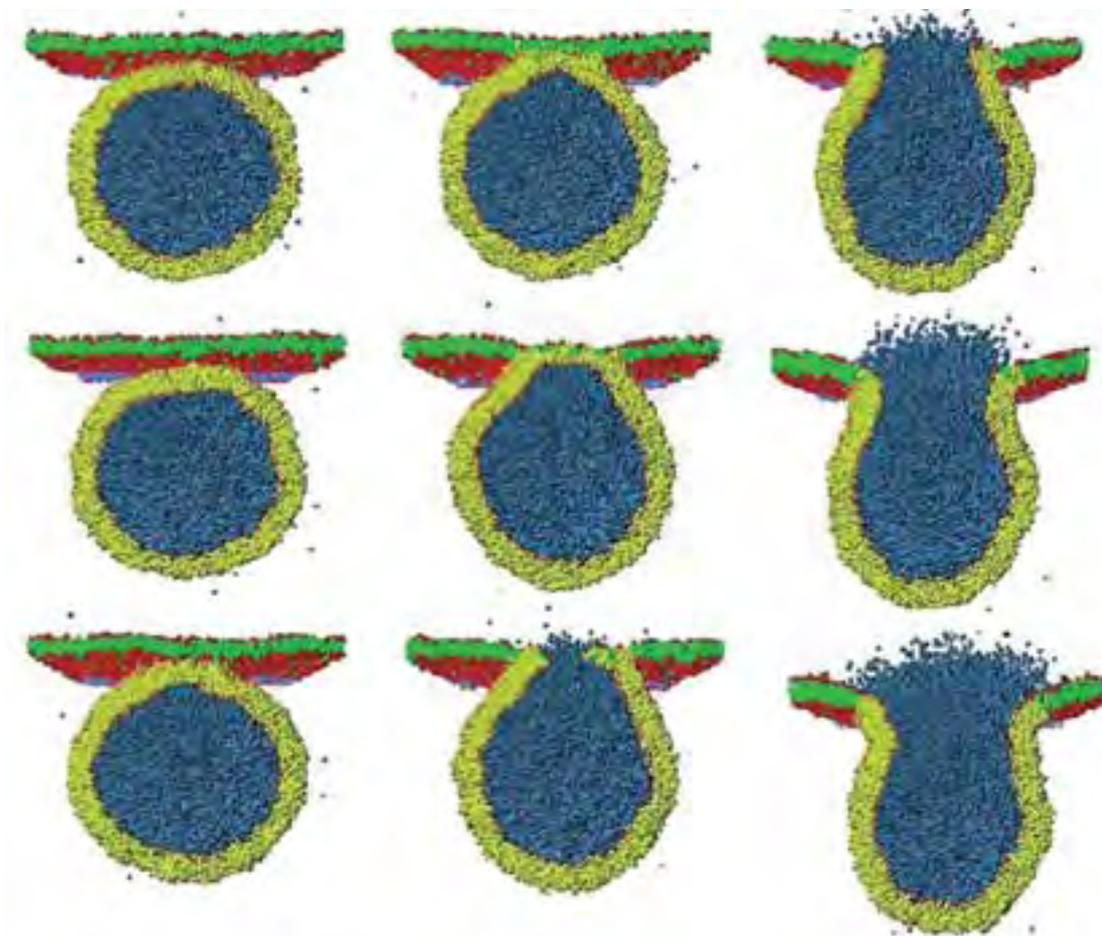


Fig. 1: Sequence of snapshots of vesicle fusion. A side view of a cut through the axis of the vesicle is shown. Water molecules exterior to the vesicle are not shown for clarity. The same lipids are used for the vesicle and planar bilayer but are colored differently for display. The vesicle diameter is approximately 50 nm and contains 6400 lipid molecules. The planar bilayer is under tension and contains 3600 lipids. The snapshots are separated by approximately 100-200 ns (not all time intervals are equal). Images produced using Pov-Ray ray tracing program: [www.povray.org](http://www.povray.org)

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# Giant Vesicles – Helping us to Understand Biological Membranes



Vesicles, or liposomes, are closed sacs made of lipid membrane encompassing fluid media. They can have sizes ranging from few tens of nanometers up to few hundreds of microns, the latter being called ‘giant vesicles’ (Fig. 1).

For the last ten years giant vesicles have been fascinating object of research for membrane scientists. Giant vesicles have the advantage of being

observable with optical microscopy. The physical characteristics of the lipid bilayer (e.g. stretching elasticity, bending stiffness, shear surface viscosity, intermonolayer slip) can be obtained from working with individual vesicles. Apart from fundamental properties of lipid membranes just mentioned above, one can study the characteristics of a multicomponent system by looking at the interactions of different molecules with the bilayer. In other words, one can bring the system closer to mimicking real cellular membranes.

One of our projects is aimed at understanding the interaction of various amphiphilic oligomers (e.g. oligooxyethylene-alkylether or C<sub>n</sub>E<sub>m</sub>) with model membranes [1]. The way we do this is by placing the membrane in a solution of molecules of interest.

A convenient technique for describing the adsorption of these molecules is Isothermal Titration Calorimetry (ITC). ITC provides a value for the strength of interaction of the molecules with the membrane (i.e. enthalpy), and the degree, to which the molecules from the bulk partition into the vesicle membrane. After adsorption, the molecules change the elasticity of the bilayer. Data for the flexibility of the membranes can be obtained by analyzing the fluctuations of vesicles [2]. Above certain concentrations, due to a drastic increase of the spontaneous curvature, C<sub>n</sub>E<sub>m</sub> induces biomimetic events such as budding of vesicles analogous to exocytosis (Fig. 2).

On the other hand, when polymers of high molecular weight, i.e., longer backbone, are anchored to the membrane, a quantitatively different effect is expected. Theoretical calculations [3] predict two regimes, mushroom and brush regime, in the dependence of the membrane stiffness on the surface concentration of anchored molecules. To verify the predictions of the model, we study membranes decorated with long  $\gamma$ -phage DNA molecules (PhD project of Vesselin Nikolov). The free end of the anchored molecule locally exerts an entropically induced pressure changing the curvature of the membrane (Fig. 3).

Bilayer composition may also lead to heterogeneous curvature due to formation of domains [4] as found in biological membranes. Lipid domains referred to as “lipid rafts” are present in the external leaflet of plasma membranes. The rafts are believed to play a significant role in cellular signal transduction. We are interested in raft formation driven by the phase behavior of lipids within the membrane. The primary objective of this study (postdoctoral project of Jeremy Pencer) is to measure the effect of membrane curvature on domain formation in vesicles composed of lipid, cholesterol and sphingolipid.

Adhesion of membranes is essential for processes like tissue formation and cellular transport.

We use vesicles on chemically structured surfaces to study adhesion (Fig. 4). Unusual morphologies and shape transitions are expected to take place in vesicles adhering to such surfaces (PhD project of Xinzhao Zhang).

We use surfaces with adhesive domains of lateral dimension in the micrometer range. Our aim is to study: (i) the effect of the domain geometry on the vesicle shapes, and (ii) morphological transitions of the adhered vesicles induced by means of change in an external parameter (e.g. osmotic pressure, temperature, surface tension).

Apart from studying adhesion of vesicles on surfaces, we are also interested in adhesion between membranes. Adhesion and fusion of membranes is essential for cellular processes like compartmentalization, import of foodstuffs and export of waste. Endo- and exocytosis involve fusion and fission of membranes. Such processes are usually triggered by external agents. An appealing approach to study these events is, first, to characterize the conditions necessary for adhesion of pure lipid membranes, and then to consider what function is to be attributed to fusogenic agents (PhD project of Christopher Haluska).

Using micromanipulation two vesicles aspirated in glass capillaries are brought together. Measurement of the contact angle between the two opposing membranes allows us to estimate the adhesion energy associated with such an event. In addition, incorporation of fusogenic agents (molecules synthesized by the group of Valerie Marchi-Artzner, College de France, Paris) which are anchored in the membrane promote fusion of the lipid bilayers. The fusogenic (sticker) molecules form complexes with trivalent metal ions in 2:1 sticker to ion ratio. When an ion binds two stickers from opposite bilayers the complex should keep the membranes close enough together for fusion to be feasible (Fig. 5).

The main barrier for fusion processes to occur is the difficulty to expel the water layer between the two adhering membranes. In our case this is overcome by the formation of metal ion complex.

Metal ions by themselves are another factor that have a significant influence on membrane functioning. Some divalent cations, e.g. Ca<sup>2+</sup>, play an important role in the regulation of biological processes such as fertilization,

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muscle contraction and signaling. Some trivalent ions were found to induce adhesion of pure lipid membranes [5]. Different salts were found to influence the solubility of proteins, so called Hofmeister effect. In some cases, the underlying mechanism causing these effects is the interaction of the ions with water: hydration, formation of water separated ion couples etc. This amounts to changing the water structure essentially by disrupting or forming hydrogen bonds. We intend to characterize the effect of different ions using ITC (PhD project of Cornelia Sinn). This technique will allow us to estimate the enthalpies associated with the mentioned above processes occurring in pure water/ions system and then compare their influence when vesicles, proteins or polymers are present in the system.

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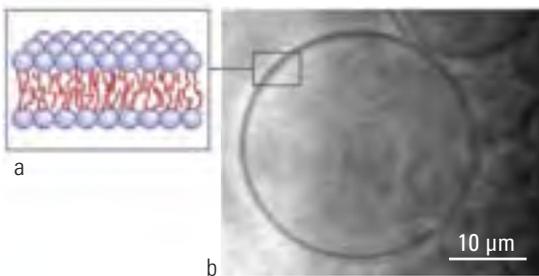


Fig. 1: a) Lipid bilayer. b) Phase contrast image of a group of giant vesicles.

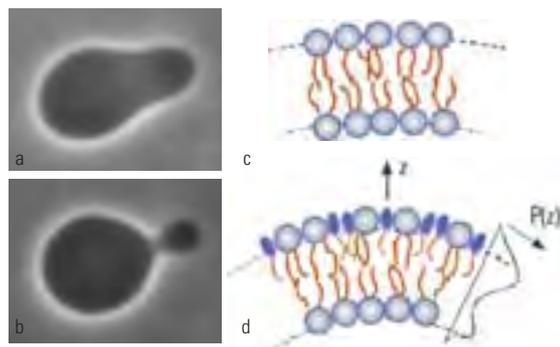


Fig. 2: a), b) Budding of a vesicle induced by adsorption of  $C_{13}E_{10}$ . c), d) Insertion of  $C_{13}E_{10}$  into the external leaflet of the vesicle membrane induces a drastic change in the bilayer spontaneous curvature.

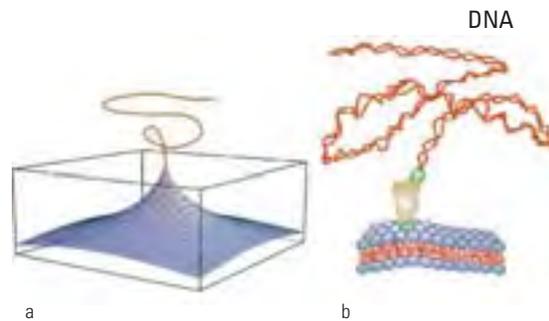


Fig. 3: a) Anchored polymer causes catenoid-like bending of the membrane (taken from [3]). b) The experimental "modeling" is done by attaching a long DNA (polymer) to a neutral lipid membrane via avidin-biotin linkage.

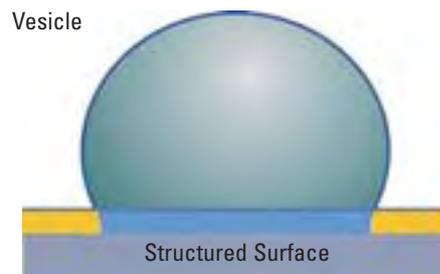


Fig. 4: Negatively charged vesicle adhering onto chemically modified glass surface. The substrate has hydrophilic positively charged domains (blue) surrounded by hydrophobic surface (yellow).

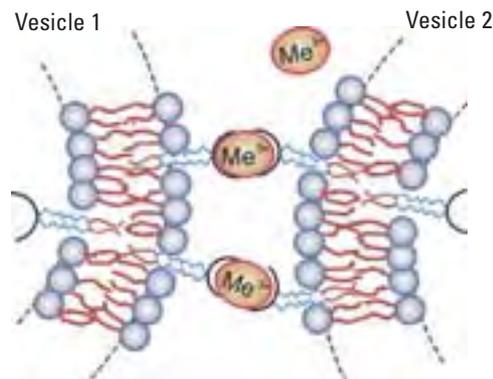


Fig. 5: Schematic presentation of two membranes brought together by sticker (or 'fusogenic') molecules that form complexes with trivalent metal ions.

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# New Membrane Physics with Polymersomes



Under appropriate conditions, amphiphilic molecules form bimolecular sheets in aqueous solution. Among such systems, especially lipid membranes have been of central interest for decades in biophysics due to their basic structural and functional role in living cells. Over the last 20 years, we have seen a steady growth in the number of researchers in the soft matter community working on

all aspects of membrane physics. Indeed, membranes have been one of the driving subjects of soft matter as a field [1]. Our contribution in this respect has been in the morphology of giant vesicles [2]. These are closed membrane bags with a typical size on the order of 10 micrometers.

Polymers define another flourishing area of soft matter. In particular, block copolymers have been recognized as versatile designer soft materials [3]. In aqueous solution, amphiphilic diblock copolymers form an amazing variety of morphological structures [4] on the nanometer scale. Recently, giant vesicles made from diblock copolymers, so called polymersomes, could be prepared [5], combining the active fields of polymer and membrane physics into a new promising research direction.

We have looked at the elastic and viscous properties of polymersomes made of polybutadien-b-polyethyleneoxide (PB-PEG) [6]. Just like lipid molecules, these amphiphiles self-assemble into bimolecular sheets with a thickness of a few nanometers. Whereas bending and stretching elastic properties of these novel membranes are found to fall in the range typical for lipid membranes, polymer membranes do exhibit a surface viscosity at room temperature which is about three orders of magnitude larger. Moreover, they are generally much tougher than lipid membranes; i.e., they have a higher lysis tension. They are very stable and easy to work with, which makes them interesting for biotechnological applications; e.g., they could be used for drug and gene delivery or chemical containers, in general.

In our polymersomes we find hexagonal superstructures (Fig. 1 and 2) which exhibit a high genus topology [7]. The vesicle polymer membranes swollen in sucrose/glucose solution are organized in concentric double bilayers. The interior and exterior of such a vesicle is connected by double membrane passages forming a hexagonal lattice. Note, that these passages are not holes in a single bilayer. The membrane shape is determined by the minimal bending elastic energy of the bilayer [1]. Theoretical shapes can be classified in a morphological phase diagram corresponding to the experimental shapes found (Fig. 2) [7]. It is remarkable that such superstructures form on a micrometer scale. Indeed, typical polymer morphologies were so far reported to be in the nanometer domain [3, 4]. Our finding opens a new avenue towards integration of structuring materials from small to large scales.

PB-PEG membranes exhibit a well defined thermal response, albeit with much slower time scales as lipid membranes at room temperature [6, 8]. Fig. 3 shows the typical relaxation behavior of tubular polymersomes after sudden temperature changes. The observed slow budding of polymer tubes after thermal quench is reminiscent of membrane pearling [9], which is induced by membrane tension. However, in our system, the vesicle volume and area stay constant, i.e., tension is not fixed. The morphological change can be explained in terms of a shape transition into a multi-bud configuration induced by an increase in the spontaneous curvature of the membrane [8].

The slow dynamics reflect the high membrane surface viscosity [6], which leads to internal rather than hydrodynamic dissipation. Thus, dynamic correlation functions of thermal shape fluctuations exhibit new interesting scaling behavior.

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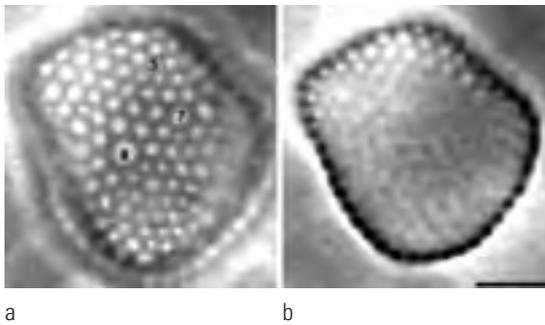


Fig 1: High genus polymersome. The top view (a) shows an optical phase contrast micrograph of a typical hexagonal lattice of passages in a double bilayer vesicle surface. Note the  $n$ -fold defects in the hexagonal lattice. The cross section (b) of the same polymer vesicle shows nearly circular tubes forming the double bilayer surface. The scale bare corresponds to  $10\ \mu\text{m}$ . Figure taken from [7].

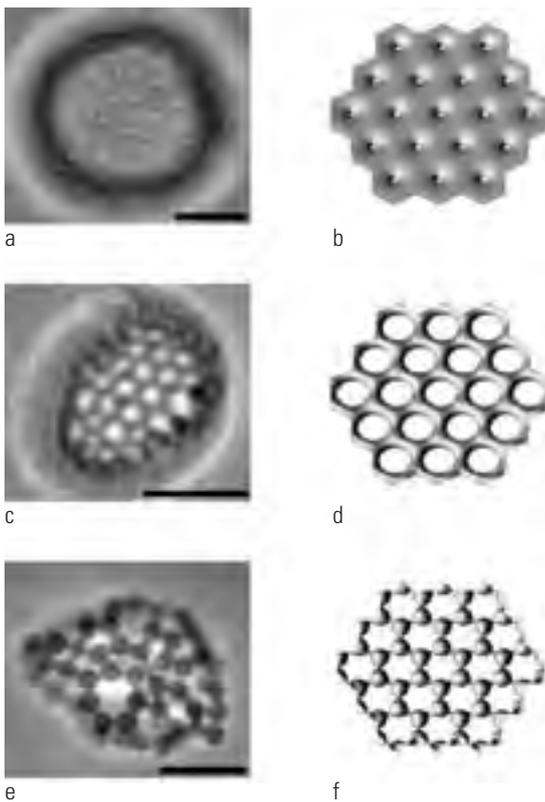


Fig 2: Comparison of experimental and theoretical lattice shape classes. The scale bar corresponds to  $10\ \mu\text{m}$ . Theoretical shapes were obtained via direct minimization of membrane bending energy. Figure adapted from [7] connected by double membrane passages forming a hexagonal lattice.

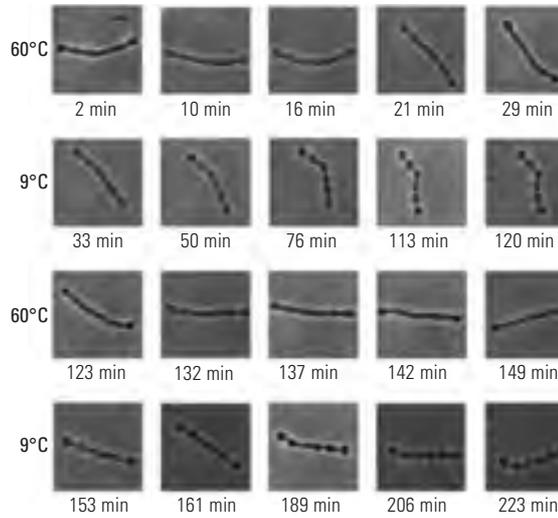


Fig 3: Reversible budding of tubular polymersomes induced by thermal cycling between  $9$  and  $60\ ^\circ\text{C}$ . Snapshots were obtained at times noted below each frame. Figure taken from [8].

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# Emmy Noether Junior Research Group



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The main interest of our group is the role which material properties play for the functioning of biological cells. In particular, we are interested in the role of forces and elasticity in cell adhesion. Other interests of our group relate to the theoretical understanding of biomaterials. For example, we investigate the structural properties of spatially extended structures in lipid-water mixtures.

## Forces and Elasticity in Cell Adhesion

It is well known, especially in the medical community, that mechanical input is essential for proper functioning of certain cell types, including tissue cells from bone, lung and blood vessels (which under physiological conditions are subject to permanent strain through body movements, breathing and blood pulsation, respectively). During the last year, there has been a large effort to clarify the underlying mechanisms on the level of single cells. It is now clear that most adherent cells not only react to external force in a specific way, but also that cells actively exert force on their environment in order to probe its mechanical properties (active mechanosensing).

For cells adhering to extracellular matrix, the force transmitting sites of adhesions are the so-called focal adhesions. In collaboration with cell biologists at the Weizmann Institute in Israel, we were able to show that internally generated force and lateral size of focal adhesion correlate in a linear way, with a stress constant of  $5.5 \text{ nN}/\mu\text{m}^2$  [1]. For this study, we developed a new technique to reconstruct forces at single focal adhesions from the deformations of a micro-patterned elastic substrate, namely by numerically solving the ill-posed inverse problem of linear elasticity theory [2]. **Fig. 1** shows the reconstructed forces exerted by a fibroblast at fluorescently labeled focal adhesions.

Since elastic deformations are long-ranged and sensitively depend on boundary conditions of the surrounding medium, cells might sense external perturbations, mechanical activity of other cells or geometrical features like boundaries through local mechanosensing. Using defect theory and linear elasticity theory, we developed several models for cell organization in soft media [3, 4]. Force patterns of polarized cells are typically pinch-like and can be modeled as anisotropic force contraction dipoles. The surrounding medium is assumed to behave like an isotropic elastic medium, which applies to many synthetic elastic substrates and which is expected to be a good approximation for hydrogels on large time and length scales. For the cellular reaction to strain, in one model we assumed that the cells react like inert physical particles [3]. This case might apply to artificial cells with a contractile system but without biochemical regulation. We found that cellular structure formation is similar

to the case of electric quadrupoles, with neighboring cells orienting perpendicular to each other. In order to model the behavior of cells with regulated response, we started from the observation that growth of focal adhesions might be triggered by a threshold in force. Since build-up of force is more efficient in a stiff environment, we suggested that cell processes are favored which proceed in a direction of large effective stiffness [4]. We found that in this case, cells line up in strings, exactly as observed experimentally. In regard to boundary effects, we were able to show that cells align perpendicular and parallel to clamped and free boundaries, respectively, again in excellent agreement with experimental observations (**Fig. 2**).

## Cubic Phases in Lipid-Water Mixtures

Different ordered phases are known to form in lipid-water mixtures, including lamellar, hexagonal and cubic bicontinuous phases. The cubic phases have been found to form in many membrane-rich regions of cells and are used for crystallization of membrane proteins. In a bicontinuous structure, one highly convoluted interface spans the whole sample, thereby dividing it into two separate labyrinths [5]. Since surfaces with vanishing mean curvature (minimal surfaces) minimize the bending energy of lipid bilayers, triply periodic minimal surfaces are the main structural models for ordered bicontinuous phases in lipid-water mixtures. Here the mid-surface of the lipid bilayers corresponds to the minimal surface, while the neutral surfaces of the two lipid monolayers correspond to parallel surfaces to the minimal surface (**Fig. 3**).

Although there are a large number of different cubic minimal surfaces, in lipid-water mixtures only the structures G, D, P and I-WP have been identified experimentally [5]. In our theoretical work, we showed that phase behavior is determined by the distribution of Gaussian curvature over the minimal mid-surface. In detail, we found that the relative stability of the different cubic phases is determined by the dimensionless quantity  $\Delta$ , which characterizes the width of this distribution [6, 7]. G, D and P have the same small value of  $\Delta$  because they belong to the same Bonnet family. I-WP has a larger value and thus needs stabilization through additional physical mechanisms to become stable. All other structures have even larger values, which explain why they are not observed in experiments. Moreover, we found that the sequence of phases with increasing water content is determined by the dimensionless topology index, which describes the porosity of the structure. This explains the generic sequence G – D – P found in experiments when increasing water content.

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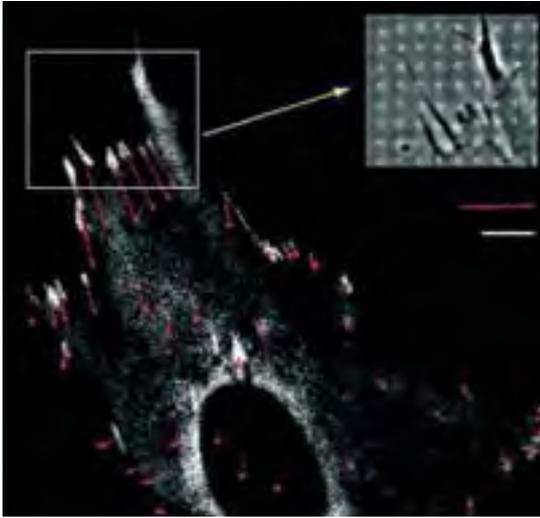


Fig. 1: Forces (red) exerted by an adhering fibroblast at sites of focal adhesions (white) which are fluorescently labeled. The inset shows a phase contrast image of the deformation of the micro-patterned elastic substrate (green), from which the force pattern has been calculated. White bar = 4  $\mu\text{m}$ , red bar = 30 nN.

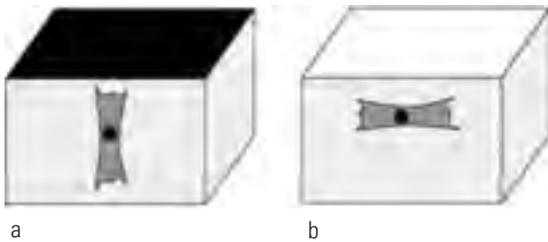


Fig. 2: Mechanically active cells in soft media align (a) perpendicular to clamped boundaries and (b) parallel to free boundaries, because in this way, they sense an effective increase in stiffness, which is favorable for growth of focal adhesions.

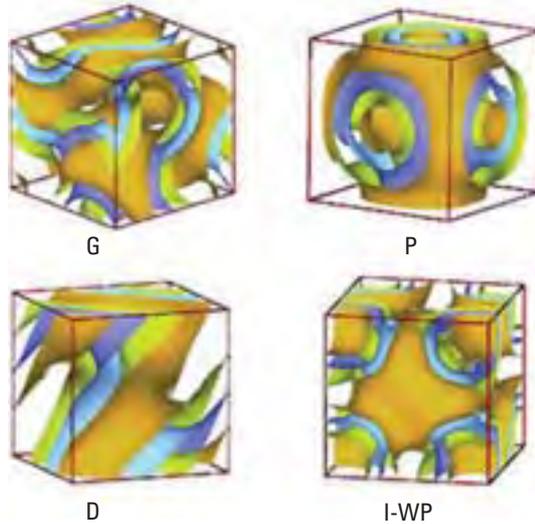


Fig. 3: Models for cubic bicontinuous phases in lipid-water mixtures: the mid-surface of the lipid bilayer is a triply periodic minimal surface (blue). The two parallel surfaces are the neutral surfaces of the lipid monolayers (orange).

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# Adhesion Behavior of Vesicles at Finite Temperature



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Biological cells are the fundamental building blocks of living organisms. The investigation of cell properties is essential for the principal understanding of life species as well as for the progress of medical technology in fields like cancer therapy or the development of more effective drugs and drug delivery methods, to name just two application areas.

A biological cell is surrounded by a closed membrane surface that serves as an interface to the outside world. The membrane is typically fluid and may consist of various components. The bending rigidity of the membrane and the molecular interaction with external substances have an important influence on the cell morphology and the cell's adhesion behavior. The adhesion of a cell to an external substrate is of special interest with respect to implantation technology.

In many cases cells act very similar to vesicles, which are homogeneously filled membrane shells. Vesicles serve as simple, well determined model systems of cells. This text describes a simulation based analysis of the adhesion of vesicles [1].

In the simplest case a vesicle membrane is a one-component double layer of identical lipids.

The membrane area can be assumed to be almost incompressible. Then, the membrane material can be characterized by its bending rigidity  $\kappa$  and the spontaneous curvature  $C_0$  only. Molecules larger than water have an extremely low probability to permeate the membrane, so that concentration gradients across the membrane lead to an osmotic pressure  $P_{os}=T(n_{in}-n_{out})$ . If (in and outside of the vesicle) there is a high concentration  $n$  of sugar molecules the vesicle volume is almost fixed at a value for which  $n_{in}=n_{out}$ . If the concentration is very low, the osmotic pressure can be neglected.

We consider the low concentration scenario and exclude any spontaneous curvature,  $C_0=0$ . Then, the behavior of a free vesicle is solely determined by the bending rigidity.

The higher the bending rigidity  $\kappa$  of the vesicle is, the more it resembles a sphere, which is the global minimum shape with respect to the elastic energy. Entropic fluctuations result for lower  $\kappa$  in a more flaccid and oscillatory surface membrane.

A vesicle close to a solid substrate may be exposed to sundry attractive and repulsive forces [2]. In any case two important forces (Fig. 1) are always present:

- The attractive van-der-Waals force between the lipid heads and the substrate atoms;
- An effective, fluctuation induced force which is repulsive and arises from the entropy based collisions of the fluctuating membrane against the substrate.

For a membrane in front of a hard wall the potential  $V_H$  of the fluctuation induced force is proportional to  $V_H \sim T^2/\kappa z^2$ , where  $z$  is the distance to the wall.

The adhesion behavior of the vesicle is influenced by the bending rigidity in the following way: An adhered vesicle with a high  $\kappa$  has almost the shape of a sphere, and so the contact area is almost zero.

For lower  $\kappa$  the global shape of the vesicle changes such that the contact area, i.e. the amount of membrane matter within reach of the attractive substrate potential, increases [3]. Consequently, the total negative adhesion energy decreases; at the same time the repulsive fluctuation induced force increases (Fig. 2, Fig. 3). For large  $\kappa$  the fluctuations are of minor importance. For small  $\kappa$  the contact area is bounded by its maximum (which is half of the total membrane area) while the fluctuating force increases like  $\kappa^{-1}$ . Thus, there should be a certain  $\kappa$  in between at which the adhesion energy is minimum. Indeed, such a minimum could be found.

With the help of Monte-Carlo simulations the behavior of a one-component vesicle adhered to a substrate was investigated. The simulations allow a study of the average adhesion behavior of a membrane in the canonical ensemble.

The vesicle membrane was treated as a smooth closed surface that was mimicked by a flexible triangulation. The mechanical properties of the membrane were resembled by a discretized elastic energy and the tethered beads model [4]. For the interaction with the wall a (10,4)-Lennard-Jones potential was used. The substrate was taken to be smooth and parallel to the  $z=0$ -plane.

The Plot in Fig. 4 shows the average adhesion energy of a vesicle as a function of its bending rigidity. In accordance with the considerations above, the plot has a minimum. Left of the minimum  $\kappa \approx 3$  the adhesion energy  $E_{wall}$  is dominated by fluctuation based forces. For  $\kappa > 3$  the decrease of the contact zone is responsible for the increase of  $E_{wall}$ .

The plot in Fig. 5 gives a deeper insight into the system. For this plot the space in front of the substrate is divided into layers of distance  $(z, z+dz]$ .

The plot shows the amount  $\rho_m(z)$  of membrane matter that lies within each of these layers, i.e. the lipid density integrated over  $x$  and  $y$ .

The separation from the substrate is given in units of the distance  $z_{min}$ , the distance where the Lennard-Jones potential is minimum. The plot focuses only on the important part of the vesicle close to the wall. In fact,  $\rho_m(z)$  does not become zero up to values of  $z=15 z_{min}$  and higher, far out of the region shown in Fig. 5. The amount of membrane matter in the region near the wall increases with decreasing  $\kappa$  corresponding to an increase of the contact area. At the same time the density distribution gets broader which indicates an increase of fluctuations. Finally, for  $\kappa=2kT$  the total amount of matter in the observed region is larger than that for  $\kappa=7.5kT$  but it is distinctly more spread out, and the peak at  $z_{min}$  is lower than the peak for  $\kappa=7.5kT$ . This means, for entropic reasons parts of the membrane in the contact area are pushed away from the optimum distance from the wall.

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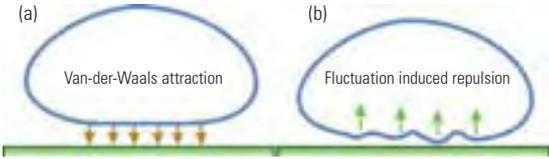


Fig. 1: Adhered vesicles are exposed to (a) van-der-Waals attraction and (b) effective repulsion induced by fluctuations.

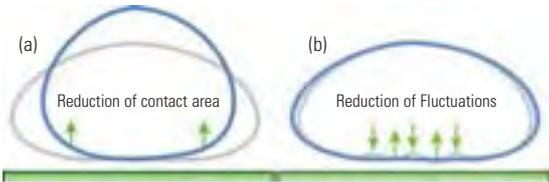


Fig. 2: If  $\kappa$  is increased, (a) the contact area shrinks, (b) the fluctuations are reduced.



(a)



(b)



(c)

Fig. 3: Snapshots of adhered vesicles with (a)  $\kappa=3kT$ , (b)  $\kappa=15kT$ , (c)  $\kappa=40kT$

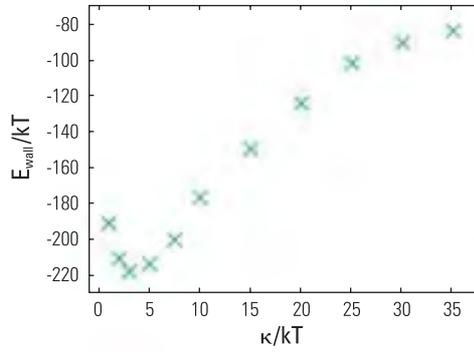


Fig. 4: Adhesion energy of an adhered vesicle as a function of the bending rigidity.

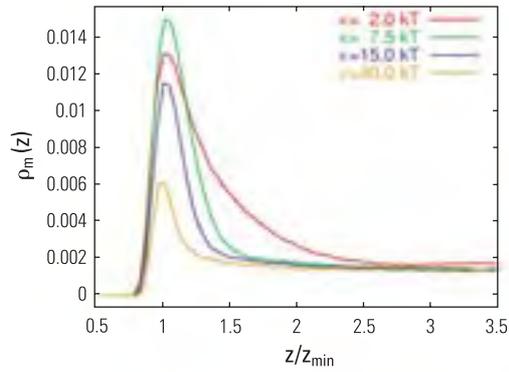


Fig. 5: Amount of membrane matter  $\rho_m(z)$  in layers of distance  $z$  from the substrate

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# Membrane Adhesion



The adhesion of cells plays a key role in important biological processes such as tissue development and immune response. The highly selective interactions leading to cell adhesion are mediated by a variety of specific receptors which are embedded in the cell membranes. The bound receptor-ligand pairs of opposing cells are often arranged into supramolecular patterns which show a complex evolution during cell adhesion.

For some biological processes, the formation of these patterns seems to be a central event in cell activation. For example, the immune response of T lymphocyte and natural killer cells to target cells is triggered by the formation of characteristic patterns at the cell-cell junction.

We have developed a statistical mechanical model for the adhesion of multicomponent membranes with adhesive receptors (stickers) and repulsive macromolecules (repellers). The repellers mimic the glycocalyx of the cell, imposing a steric barrier for the adhesion. This barrier strongly affects the equilibrium phase behavior and the adhesion dynamics of the membrane. The unbinding transition is continuous for weak barriers, and discontinuous for strong barriers [1, 2].

To model the adhesion dynamics of a cell, we consider a membrane consisting of a circular contact area surrounded by nonadhering area in which the membrane is not in contact with the second membrane [3]. We find distinct dynamic regimes of pattern formation depending on the characteristic lengths and the concentrations of stickers and repellers: (A) Long repellers impose a strong barrier to sticker adhesion. The nucleation time for sticker binding therefore is large compared to typical diffusion times, and the membrane binds via growth of a single sticker nucleus; (B) For short repellers, the nucleation time for sticker binding is small, and many nuclei of bound stickers are formed initially. Due to the diffusion of stickers into the contact area, nuclei at the rim of this area grow faster, and at sufficiently high sticker concentrations, a ring of bound stickers is formed which encloses a central domain of repellers, see Fig. 1 below. At later times, this pattern inverts, and a central sticker cluster is surrounded by repellers. The sequence of patterns in this regime has a striking similarity to the pattern evolution observed during T cell adhesion; (C) In an intermediate regime, the sticker concentration is not large enough for the formation of a closed sticker ring from the initial nuclei. Instead, circular arrangements of separate sticker clusters emerge.

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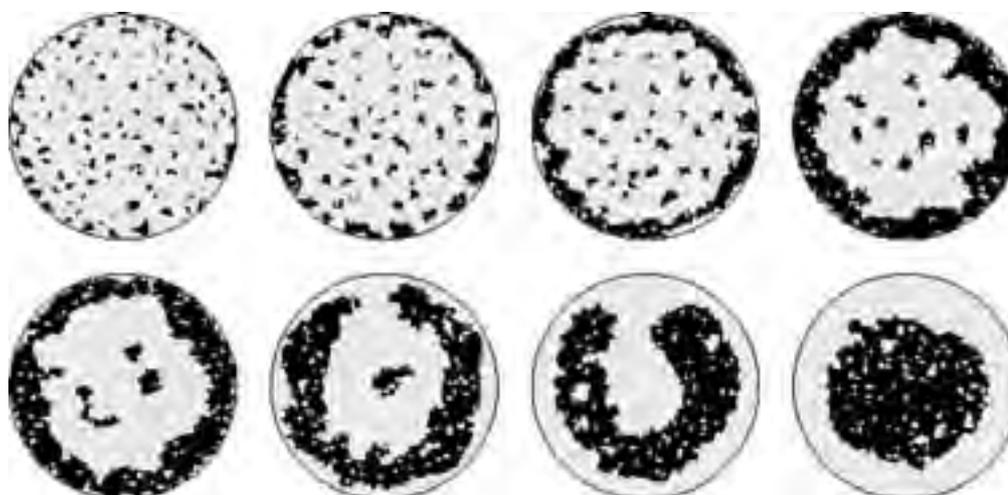


Fig. 1: Time sequence of MC configurations for the contact area. Stickers are shown in black, repellers in grey. Due to the diffusion of stickers into the contact area, clusters at the rim grow faster, forming rings at intermediate time scales. The final configuration represents the equilibrium state.

# Protein Folding Kinetics

What are the rates and routes of folding of 2-state proteins? 2-state proteins are relatively small proteins that fold and unfold with single-exponential kinetics, and so can be modeled in mass-action kinetics using only two states, D (denatured) and N (native). An important recent observation is the correlation found by Plaxco et al. [1] between the folding rates of 2-state proteins and the 'topology' of their three-dimensional structures. Plaxco et al. quantified the topology by the average contact order (CO), the average sequence separation  $|i-j|$  between all monomers  $i$  and  $j$  in contact in the folded structure. Proteins with predominantly local contacts have a small average CO (e.g.,  $\alpha$ -helical proteins) and fold faster than proteins with many nonlocal contacts having a larger average CO (e.g.,  $\beta$ -proteins).

We have developed a simple model to calculate the folding rates and routes of 2-state proteins from the contact maps of their three-dimensional structures [2,3]. The model is based on the graph-theoretical concept of effective contact order (ECO). The ECO is the length of the loop that closes to form a contact between two monomers, for a chain with a given set of contacts. More precisely, the ECO is the number of steps along the shortest path on the polymer graph between two monomers  $i$  and  $j$  for a chain in a given configuration. While the CO is independent of the folding path, the ECO is dependent on the folding routes and therefore gives information about the mechanism of folding.

We find that proteins fold in general along opportunistic zipping routes in which each step in folding involves only a small loss of conformational entropy. The ECO provides a way to calculate this conditional conformational entropy loss for each zipping step. In short, while there are many routes that a protein can follow to lower its energy, we find that only a very small fraction of those routes are low-entropy-loss routes, and hence are predicted to be the dominant folding routes.

An example is shown in Fig. 1. The three-dimensional structure of the Chymotrypsin Inhibitor 2 (CI2) consists of a four-stranded  $\beta$ -sheet packed against an  $\alpha$ -helix. The contact map of CI2 has four major contact clusters corresponding to the  $\alpha$ -helix and the  $\beta$ -strand pairings  $\beta_2\beta_3$ ,  $\beta_3\beta_4$ , and  $\beta_1\beta_4$ . The strand pairing  $\beta_1\beta_4$  involves highly nonlocal contacts between the two ends of the chain, and therefore turns out to be the folding bottleneck. However, we find that only a relatively small loop has to be closed if  $\beta_1\beta_4$  folds after the other three major clusters  $\alpha$ ,  $\beta_2\beta_3$ , and  $\beta_3\beta_4$ . On this dominant low-entropy-loss route, all major clusters are involved in the rate-limiting bottleneck, the formation of the  $\beta_1\beta_4$  strand pairing. Therefore, this route rationalizes the experimental observation that mutations along the whole protein chain affect the folding rate of CI2.

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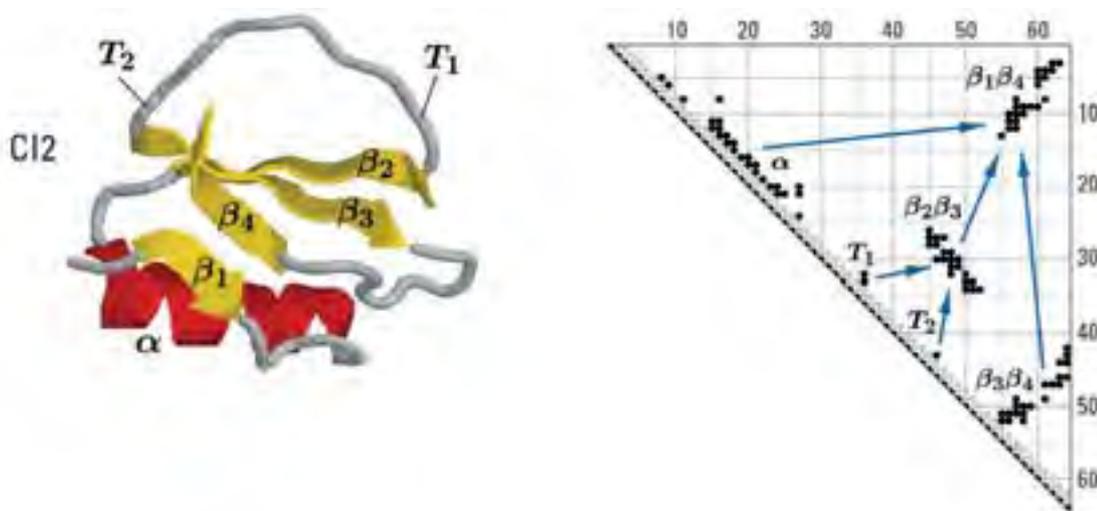
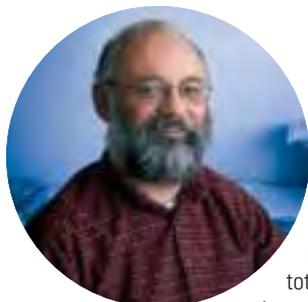


Fig. 1: Left: Structure of the Chymotrypsin Inhibitor 2 (CI2). --- Right: Contact map with dominant folding route for CI2.

# Polyelectrolytes



## Annealed Polyelectrolytes

'Weak' polyelectrolytes as, e.g., poly(acrylic acid) dissociate in a limited pH range. The average degree of dissociation  $\langle f \rangle$  is determined by the pH of the solution which, in physical terms, corresponds to the chemical potential  $\mu$  of the charges. Because the total number of charges as well as their positions along the chain are fluctuating, such polymers are also called 'annealed' polyelectrolytes.

**Θ and good solvent:** A charge accumulation appears at the chain ends within a size of the order of the screening length  $\lambda_D$ . The equilibrium charge distribution  $f(s)$  on a flexible chain was given in ref. [1]. To check the theoretical prediction we started with a simulation model chosen as close as possible to that used in theory where the charges are assumed to interact by a screened Coulomb potential. We study annealed polyelectrolytes by semi-grand canonical Monte Carlo simulations where the chain is in contact with a reservoir of charges of fixed chemical potential  $\mu$ . **Fig. 1** shows the charge distribution obtained in simulations together with the theoretical prediction. In a fairly wide parameter range, we observe almost perfect agreement [2].

**Poor solvent:** Additionally to the model used for  $\Theta$  solvents, a short-ranged attractive potential is included. To scan properly the phase space in the case of globular structures, additional kinds of Monte Carlo moves are added. Polyelectrolytes in poor solvent are known to be unstable to the so-called pearl-necklace conformation. For annealed polyelectrolytes, however, the pearl-necklace structure itself becomes unstable if the solvent is too poor. (The solvent quality is measured by the normalized distance from the  $\Theta$  point  $\tau$ .) Upon increasing the charge, the polyelectrolytes are expected to show a discontinuous transition between a collapsed globular conformation and a stretched one. In the simulations this transition is seen in a quite large parameter range (**Fig. 2**) [3]. Only in a rather limited region, in particular at small Bjerrum lengths  $\lambda_B$ , we obtain pearl-necklaces. In **Fig. 3** a dumbbell-like structure is shown.

## Polyelectrolyte Brushes

Polymer brushes are systems in which chains are attached by one end to a surface in a way that the grafting density is high enough to enforce stretching of the chains away from the surface resulting in a brush-like conformation. Polyelectrolyte brushes constitute a new class of materials which has recently received considerable interest. Here we report two novel brush regimes first obtained by simulation studies on polyelectrolyte brushes. The new features not predicted by previous theories stimulated a better theoretical understanding of this class of polymers.

**Collapsed brush regime:** At moderate interaction strength  $\lambda_B=0.7b$  we observe a new collapsed regime where the monomer density becomes independent of the grafting density resulting in a linear scaling of the brush height with  $\rho_a$  [4] (**Fig. 4**). Including electrostatic correlations, which cause an attractive interaction, the nature of the collapsed regime can be understood within an extended scaling model [5]. The resulting phase diagram is shown in **Fig. 5**. The brush can collapse at strong coupling  $\lambda_B^3 > v_2$  and strong charging  $f > (v_2/\lambda_B^3)^{1/2}$ , with  $v_2$  being the second virial. In this phase, the brush height, resulting from a balance between steric repulsion and attractive Coulomb correlations, grows indeed linearly with  $\rho_a$ .

**Non-linear osmotic brush regime:** Reducing  $\lambda_B$  the collapsed brush regime disappears [6] as predicted by the extended scaling theory [5]. However, contrary to the scaling law of the osmotic regime, the brush height exhibits still a weak dependence on  $\rho_a$  (**Fig. 4**). Such a behavior is known to appear if the counter ion distribution extends substantially beyond the rim of the brush. Obviously, this does not happen in our case (**Fig. 4**). In all previous theoretical models it was assumed that counter ions are distributed uniformly in the lateral directions. However, inhomogeneous distributions were obtained both in experiment and simulation. Recently it has been shown that lateral inhomogeneity indeed yields a weak dependence of brush height on anchoring density [7]. The corresponding brush regime is called non-linear osmotic. In **Fig. 6** we compare simulation results with theoretical predictions obtained without any fitting parameter. Within the order of the systematic error of the model we find reasonable agreement.

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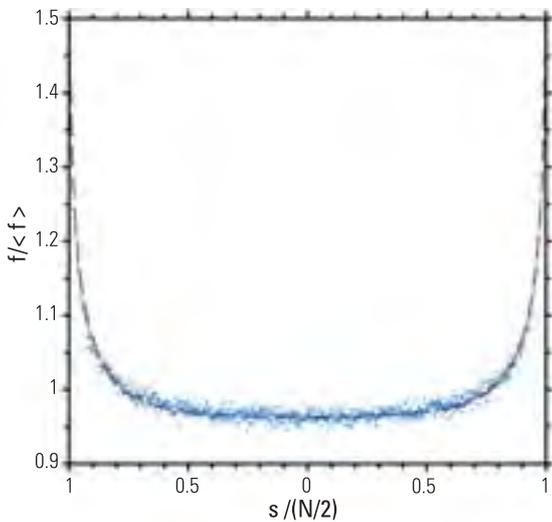


Fig. 1: Charge distribution on a Gaussian chain ( $N=1000$ ,  $\langle f \rangle=0.083$ ,  $\lambda_D=64b$ ). Theoretical results are given as dashed line, simulation data as dots.

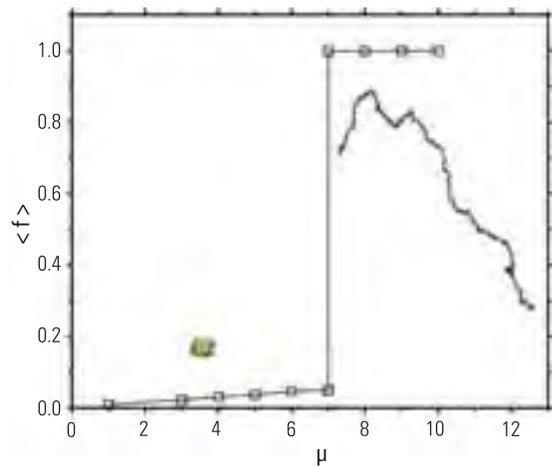


Fig. 2: Average degree of charging versus chemical potential (titration curve) for a chain of length  $N=256$  at  $\tau=0.22$ ,  $\lambda_D/b=1$ . The conformations are indicated by typical snapshots (charged monomers are colored red, uncharged ones yellow).



Fig. 3: Snapshot of a chain with  $N=256$  monomers at  $\tau=0.22$ ,  $\lambda_D/b=0.01$ ,  $\mu=6.0$ . Note that inside the pearls there are a few uncharged monomers.

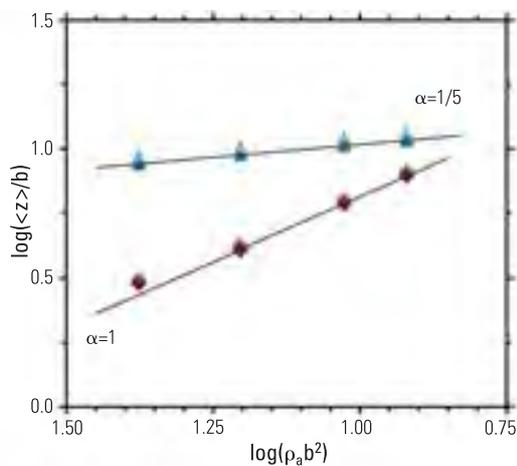


Fig. 4: Average brush height (filled symbols) and height of counterion layer (open symbols) versus grafting density. Completely charged brushes at  $\lambda_D=0.7b$  (diamonds) and  $\lambda_D=0.1b$  (triangles). The lines give power laws  $\langle z \rangle \sim \rho_a^\alpha$ .

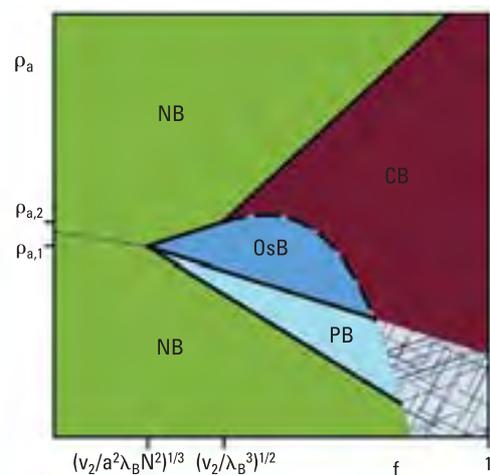


Fig. 5: Scaling theory phase diagram in logarithmic scales with quasi-neutral (NB), osmotic (OsB), Pincus (PB) and collapsed (CB) brush regimes.

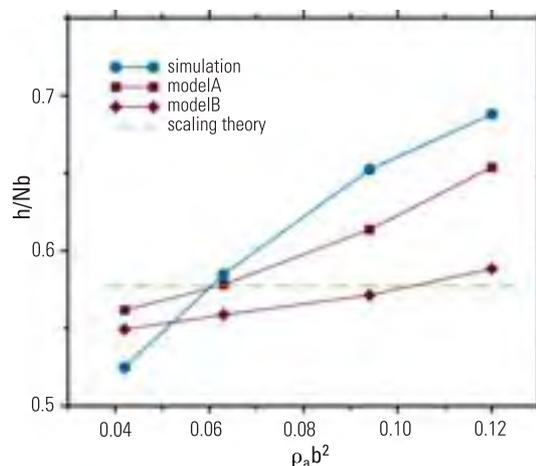


Fig. 6: Brush height versus grafting density at  $\lambda_D=0.1b$ ,  $f=1$ . Simulation data and theoretical predictions

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# Semiflexible Polymers and Filaments



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Many biopolymers such as DNA, filamentous (F-) actin or microtubules belong to the class of semiflexible polymers. The biological function of these polymers requires considerable mechanical rigidity. For example, actin filaments are the main structural element of the cytoskeleton which gives the cell unique mechanical properties as it forms a network rigid enough to maintain the shape of the cell and transmit forces yet flexible enough to allow for cell motion and internal reorganization as response to external mechanical stimuli.

The physics of semiflexible polymers is in many respects fundamentally different from the physics of flexible synthetic polymers such as polyethylene.

For semiflexible polymers not only the conformational entropy but also the bending energy plays an important role. The bending stiffness is characterized by the persistence length. On scales larger than the persistence length the polymer loses its orientation and starts to behave as flexible, mostly entropic chain whereas on smaller scales bending energy dominates and qualitatively new semiflexible behavior appears. The persistence lengths of the most prominent biopolymers range from 50 nm for DNA to the 10  $\mu\text{m}$ -range for F-actin or even up to the mm-range for microtubules and are thus comparable to typical contour lengths the polymers such that semiflexible behavior plays an important role.

Another important class of semiflexible polymers are polyelectrolytes where the electrostatic repulsion of charges along the backbone can give rise to considerable bending rigidity depending on the salinity of the surrounding solution.

Semiflexibility is also crucial for the bundling of two such biopolymers by attractive interactions as well as their adsorption onto adhesive substrates as shown schematically in **Fig. 1**. Unbundling and desorption transitions are due to the competition between the energy gained by binding to an attractive potential well and the associated loss of configurational entropy. As the bending rigidity and, thus, the persistence length is increased the entropy loss is reduced. Therefore semiflexible polymers bundle and adsorb more easily as compared to a flexible polymer.

These problems can be theoretically described as single polymer problems in the presence of an external binding or adsorbing potential. Intermolecular forces give rise to polymer/polymer or polymer/surface interactions that contain both an attractive potential well and a repulsive hard core, see **Fig. 2**. However, attraction might also depend on the orientation of polymer segments, for example, if the binding is mediated by crosslinkers.

We have studied this problem analytically solving the differential transfer matrix equation **[1]**. The transfer matrix calculation allows to obtain explicit expressions for the transition points, the order of the unbundling and desorption transition, and the critical exponents which characterize the corresponding critical behavior. Results for the critical exponents agree with renormalization group results **[2]**. The transfer matrix approach identifies up to four distinct universality classes corresponding to the four interaction potentials shown in **Fig. 2**. Somewhat surprisingly, it turns out that the orientation dependence of the attraction can influence the order of these transitions which is a distinct feature of semiflexible polymers. In 1+1 dimensions the transfer matrix approach even allows to calculate the exact distribution of polymer segment positions and orientations. We also find that the repulsive hard core part of the interaction potential becomes irrelevant in higher dimensions  $d \geq 3$ . All analytical results have been confirmed by numerical transfer matrix calculation and Monte-Carlo simulations, a snapshot of which is shown in **Fig. 3**.

Desorption does not only occur as a result of increasing temperature and thermal fluctuations but also if a desorbing force is applied to one end of the polymer, as indicated in **Fig. 3**. This force-induced desorption can be experimentally studied using single molecule AFM techniques. Using the exact transfer matrix result for the probability distribution of polymer segments the force-extensions characteristics for desorption by an applied force can be obtained. One interesting feature is the occurrence of an energetic barrier against force-induced desorption which is solely due to the effects from bending rigidity.

A bundle of three attractive semiflexible polymers (**Fig. 4**) represents a more challenging problem that can only be studied by scaling arguments and extensive Monte-Carlo simulations **[3]**. One basic question regarding bundles of more than two polymers is whether the bundling proceeds via a sequence of transitions in pairs or in a single cooperative transition. Surprisingly it turns out that the phase transition is cooperative, similar to what is shown in **Fig. 5** for identical persistence lengths, even for a wide range of different persistence lengths.

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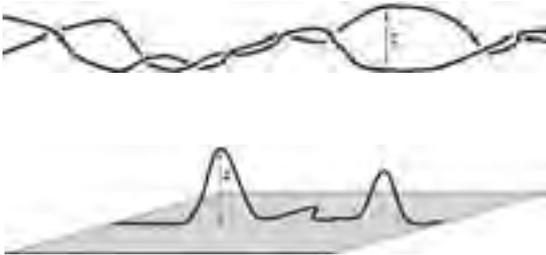


Fig. 1: Top: Bundling of two semiflexible polymers.  
Bottom: Adsorption of a semiflexible polymer onto a planar substrate.



Fig. 4: Snapshot of a Monte-Carlo simulation of a bundle of three semiflexible polymers.

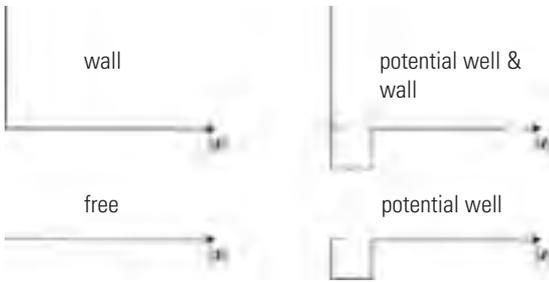


Fig. 2: Four types of interaction potentials corresponding to the four different universality classes.



Fig. 3: Snapshot of a Monte-Carlo simulation of an adsorbed polymer. A force applied to one polymer end (arrow) can lead to force-induced desorption.

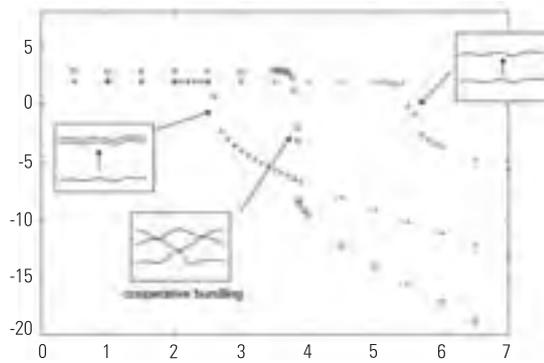


Fig. 5: Potential energy of three identical semiflexible polymers as function of attraction strength in 1+2 dimensions. The discontinuity signals the location of a (first order) bundling transition. Two subsequent transitions in pairs would give the curves on the right (circles) and on the left (triangles). The Monte-Carlo simulation shows that the actual transition is cooperative and happens along the curve in the middle (squares) before the first pair can bind.

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# Molecular Motors and Active Systems



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Our current understanding of the movements of molecular motors is based on biomimetic models systems. Prominent examples are cytoskeletal filaments such as microtubules which are immobilized onto solid substrates and which interact with mobile motor molecules such as kinesin, compare **Fig. 1**. These motors are powered by the free energy released from the exergonic hydrolysis of adenosine triphosphate (ATP). In fact, these motors are able to transform the free energy released from the hydrolysis of a single ATP molecule into mechanical work. Thus, these motors use the smallest possible amount of fuel. One such motor is kinesin, as shown in **Fig. 1**, which walks along microtubules.

This motor is observed to walk via discrete steps, the size of which is close to the repeat distance of the filament which is 8 nm. At each step, the cytoskeletal motor has a small but nonzero probability to unbind from the filament. Thus, it makes of the order of a hundreds steps before it falls off.

On larger time scales, the motor undergoes peculiar random walks which consist of alternating sequences of bound and unbound motor states, i.e., of directed walks along the filaments and nondirected diffusion in the aqueous solution.

On larger time scales, the motor undergoes peculiar random walks which consist of alternating sequences of bound and unbound motor states, i.e., of directed walks along the filaments and nondirected diffusion in the aqueous solution.

## Active Transport

In our theoretical work, the directed walks of bound motors are studied in the framework of stochastic ratchet models which are mapped onto discrete networks as shown in **Fig. 2**. These networks can have an arbitrary number of vertices but are periodic in one spatial direction which corresponds to the motor displacement parallel to the filament.

A detailed analysis of the stochastic networks reveals that they exhibit universal features. One such feature is the functional relationship between the motor velocity and the concentration of the fuel molecules. This functional dependence is primarily determined by the total number  $Q$  of unbalanced transitions present in the network. If the unbalanced transition rates obey Michaelis-Menten kinetics, one obtains general functional relationships for the motor velocity  $v_b$  on the concentration  $\Gamma$  of the fuel molecules and on the external force  $F$  as given by **[1, 2]**

$$v_b(\Gamma, F) = \left[ \sum_{n=0}^Q g_n(F) \Gamma^n \right] / \left[ \sum_{n=0}^Q h_n(F) \Gamma^n \right] \quad (1)$$

Thus, the velocity  $v_b$  can be expressed in terms of the ratio of two  $\Gamma$ -polynomials of degree  $Q$  with  $F$ -dependent coefficients.

In this way, one arrives at a classification scheme for the functional dependence of the velocity on the two parameters  $\Gamma$  and  $F$  which agrees, for  $Q=1$ , with the experimental observations on kinesin. For each value of  $Q$ , the functional relationships as given by (1) are universal in the sense that they are valid (i) for any number of balanced transition rates, (ii) for any choice of the molecular force potentials, (iii) for arbitrary load force  $F$ , and (iv) for any force dependence of the Michaelis-Menten reaction rate constants.

## Active Pattern Formation

As mentioned, the motor unbinds from the filament after a certain walking time and then undergoes peculiar random walks. A particularly interesting system, in which one can study these walks, is provided by a filament which is immobilized within a tube-like compartment as shown in **Fig. 3**. This system resembles an axon and corresponds to a finite concentration of motors in a closed tube.

In the presence of ATP, the motors move to the right (plus end of filament). As a result of this directed motion, a density gradient builds up which acts to create a diffusive backflow of unbound motors towards the left. This leads to a stationary state characterized by a nonuniform density profile for which the right part of the filament exhibits a traffic jam. These nonuniform density profiles represent simple examples for active pattern formation. **[3]**

In the stationary state, the bound and the unbound currents cancel each other. If one now studies the bound current as a function of the overall motor concentration, one finds that this quantity exhibits a maximum which reflects the presence of traffic jams for larger concentrations.

## Active Transformations

In general, an active system may exhibit more than one stationary state and may then undergo active transformations between these different states. One example for such active transformations is provided by open tube-like compartments for which the two ends are coupled to motor reservoirs with certain motor densities. As one varies these boundary densities, the system can undergo active transformations between a high-density, a low-density, and a maximal current state. **[4]**

More recently, we have found that phase transformations are also present for closed tube-like compartments which contain two different types of motors.

The concepts of active transport, active pattern formation, and active transformations are quite general and apply to a wide range of biomimetic systems with active components.

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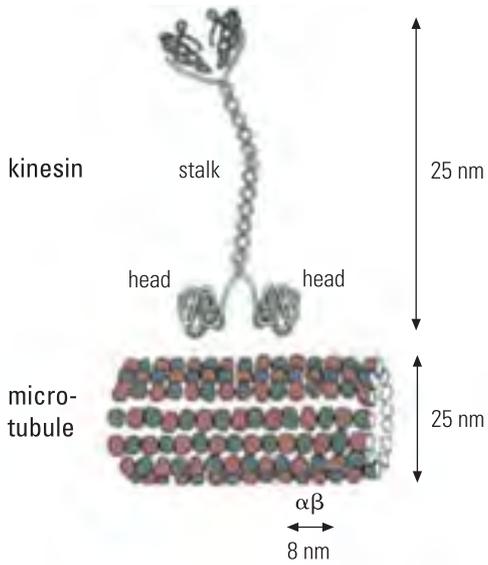


Fig. 1: The molecular motor kinesin has two motor domains or heads which can both bind to the microtubule and hydrolyse ATP.

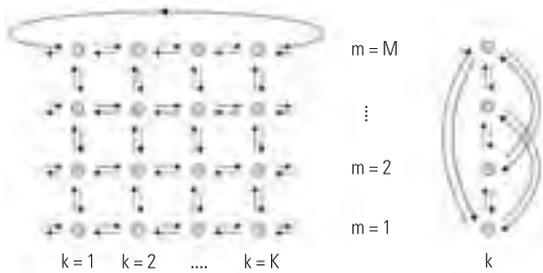


Fig. 2: Stochastic network of KM discrete motor states represented by vertices  $(k, m)$  with  $1 \leq k \leq K$  and  $1 \leq m \leq M$ . The arrows or directed edges correspond to transitions between these states (left). The network satisfies periodic boundary conditions in the longitudinal direction parallel to the  $k$ -axis; and (right) it has an arbitrary number of transverse dimensions.

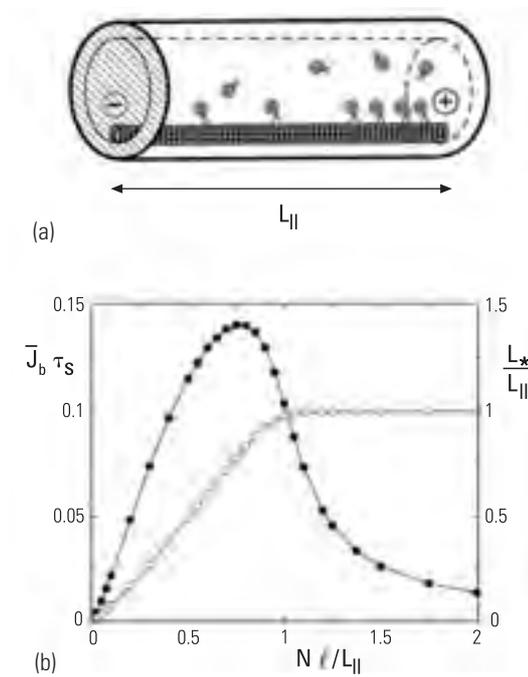


Fig. 3: (a) Closed tube with a fixed number of cargo particles. Each particle carries a certain number of molecular motors which can bind to the filament; and (b) Bound current  $J_b$  (full circles) and jam length  $L^*$  (open circles) as a function of the total number  $N$  of cargo particles. The parameters  $L_{||}$ ,  $l$ , and  $\tau_s$  are the longitudinal extension of the tube, the step length, and the step time, respectively.

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# Theoretical Evolutionary Ecology



## Evolutionary Dynamics of Single Species

One of the most studied systems in Ecology and Evolution is the biology of plant's seeds.

Seeds offer not only for their enormous social and economical relevance scientists a number of still unresolved challenging questions.

Seeds are living embryos whose development stops until favourable environmental conditions are met for germination. During their development, the mother plant makes a series of investments in terms of energy spending to produce a different number or a different quality of seeds. The amount of seeds produced and their quality are the result of an evolutionary process driven by the interaction of the species with its environment.

Just before seeds become ripe and fall down, they start a process of dehydration, which keeps their internal structure of membranes and compartments intact and at rest. When development starts again, the membranes of the seed get hydrated and oxygen flows inside. In few hours, the entire molecular machinery is at work again. Signals trigger the development which depends on the biology of the plant but also on the predictability of the environment.

The extreme case comes from plants living in a desert, where yield can vary greatly from one season to the other and sometimes no seeds at all are produced. In such environments, only those species can survive, whose seeds germinate only with a certain probability. There we speak of "delayed germination" or "dormancy" (Fig. 1).

In the desert, vegetation is limited to few months in winter, before the temperature rises so much that all plants die. Winter can be pretty good or very bad depending on whether it rains enough or not. During bad years, the plants cannot reach maturity and produce seeds. If all seeds had germinated with the first rain, a bad year would mean the extinction of that species. That is why seeds of desert plants germinate only with a certain probability, even if conditions are optimal. This ensures that permanent seed-bank remains buried in the ground and allows spreading the risk of extinction over many seasons.

Is there any rule telling us how large should be this germination probability? Early models for seed-bank dynamics [1, 2] mapped the problem onto a random walk  $X(t+1)=R(t)+X(t)$  where  $X(t)$  is the logarithm of the size of the seed bank in season  $t+1$  and  $R(t)$  contains the contributions of the weather in season  $t$  and depends on the germination fraction  $g$ .

In natural systems, morphs of the same species carrying different  $g$  struggle for the same limited resources. Any choice of  $g$  is therefore a strategy and the search is for the optimal. This occurs through an evolutionary process driven by invasion: Any resident strategy  $g$  will be threatened by the arrival of some invader  $g'$  whose seed-bank obeys the dynamic equation  $X'(t+1)=R'(t)+X(t)$  where  $R'$  will depend also on the  $g$  of the resident. The invader will be successful and replace the resident if the time-average of  $R'$  will be positive. This process will go on until a stable strategy is established, which cannot be invaded. This is the Evolutionary Stable Strategy.

This simple model for delayed germination has been very successful because it gives a clear justification of the selective advantage of a certain germination probability.

In addition, the model implied also that the seed-bank should be uniform in  $g$ . Several empirical studies however have demonstrated that the seed-bank is not homogenous. Indeed, seeds produced after very abundant good seasons have a lower germination probability than those produced after a bad and dry season.

To find out whether these results make sense, together with Dr. Katja Tielbörger of the University of Potsdam we have developed a model to prove that such kind of behavior is better than the uniform- $g$  strategy. In fact, we needed to relax the assumptions of the early models by allowing for such variability in  $g$  to appear. We have then let the system evolve and find its Evolutionary Stable Strategy, which was always with the  $g$  after a good season smaller than the  $g$  after a dry season (Fig. 2).

This kind of behavior is interpreted as a response to the expectation of a stronger competition after an abundant season. At the level of the seeds instead, this means that the plants have more resources to invest in the membranes covering the seeds when weather conditions are optimal. This poses the question of what is the chemical and mechanical basis of delayed germination, a phenomena which is still poorly understood.

## From one Species to Ecosystems

What determines the number of species, i.e. biodiversity in an ecosystem? How are these species distributed among trophic levels? What is the effect of processes like migration on this structure? How does the number of species scale with the area of the location? These are some of the questions that many theoretical ecologists, most of them physicists, try to answer by means of mathematical models and computer simulations. These are also some of the questions that arise from field ecologists interested in general trends and concepts and from environmentalists trying to find the best solution to safeguard biodiversity.

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**1992:** Diploma, Physics

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Thesis: Conformal Invariance,

Renormalization Group and Integrable Models in Two-Dimensional Quantum Field Theories

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Thesis: Form Factors and

Correlation Functions

**1996-1998:** Postdoc

(Max Planck Institute for the Physics of Complex Systems, Dresden)

**1998-2000:** Postdoc

(Max Planck Institute of Colloids and Interfaces, Golm)

**Since 2000:** Group Leader and IMPRS Coordinator (Max Planck Institute of Colloids and Interfaces, Golm)

Ecosystems are characterized by a continuous turnover of species. There are processes like immigration, which are the source of newcomers, and there is population dynamics, with competition and predation, which is the source of extinction. In any natural system therefore, biodiversity is maintained as the result of a balance between these two competing mechanisms. Any stationary structure and distribution therefore carries the fingerprint of these mechanisms.

If we see a natural community with all links connecting the interacting species, this looks like a network [3]. This kind of ecological networks are known since long for being organized in a large-scale structure like trophic levels with remarkable stability properties. In a recent attempt to connect processes to structure, together with Tiziano Zito, now at the Humboldt University in Berlin, we have developed a computer model that extends previous work [4, 5].

In this model, only the average properties in each trophic level are computed and the fluctuations around the averages are substituted by fictitious distributions.

The existence of these distributions reflects the fact that populations in the same trophic level might have (a) quite different sizes or (b) quite different predatory efficiency. In fact, both case are present in natural systems, but the advantage of the simulation is that we could take them in account separately. In case (a), are random effects that shape the size-distribution and therefore extinction is almost independent of competition. In case (b), extinction is the result of competition alone.

Coupled to a stochastic dynamics which mimics the process of immigration, the systems show remarkable differences in the two formulations.

In case (a) indeed, the stationary distribution of species in trophic levels sees the first level as the most diverse one. In this case, moreover, the total number of species  $S$  scales like  $\sim R^{1/2}$  with the extensive resources  $R$  that might represent an area. In case (b) instead, competition introduces a scale in the system and depending on the value of the other parameters, the most populated level can be higher then the first. Here the scaling with the resources is just logarithmic, in agreement with previous results [4, 5]. Fig. 3a, b is a cartoon of a possible community for cases (a) and (b) respectively. The figures show that the number of species in each level is lower in case (b) than in (a) and that in case (b) the number of levels is typically larger than in case (a).

Further developments will go in the direction of comparing these models to empirical data and molecular-data approaches.

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Fig. 1: *Senecio Glaucus*. The seeds of this species germinate only with 10-25 % probability under optimal conditions.

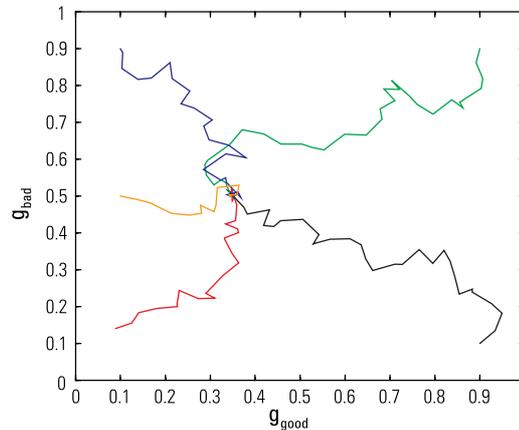


Fig. 2: All evolutionary paths lead to the same stable strategy. On the x-axis the  $g$  after a good season, on the y-axis the  $g$  after a bad season

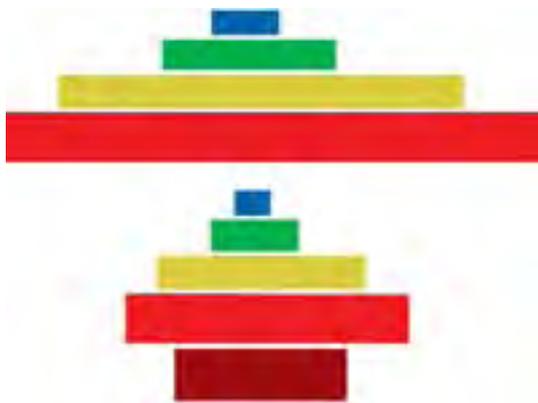


Fig. 3: a) The first trophic level is the most populated. The food-chain is short. b) The most populated trophic level is the second. The system is not very populated and the food-chain is longer.

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# BIO MATERIALS

BIOMATERIALS



# Research in the Department of Biomaterials



The Department of Biomaterials, founded 2003, will focus on interdisciplinary research on biological and biomimetic materials. The emphasis is on understanding how the mechanical or other physical properties are governed by structure and composition.

Research on natural materials (such as bone or wood) has potential applications in many fields.

First, design concepts for new materials may be improved by learning from nature. Second, the understanding of basic mechanisms by which the structure of bone or connective tissue is optimized opens the way for studying diseases and thus for contributing to diagnosis and development of treatment strategies. A third option is to use structures grown by nature and transform them by physical or chemical treatment into technically relevant materials (biotemplating). Given the complexity of natural materials, new approaches for structural characterization are needed. Some of these will be further developed in the department, in particular for studying hierarchical structures. Part of these activities have already been started at the Erich Schmid Institute of Materials Science (Austrian Academy of Science, Leoben, Austria) by the small group of scientists moving from Austria to Potsdam in 2003/2004 in order to form the initial nucleus of the Department of Biomaterials.

## Hierarchical Structure of Natural Materials

The development of metals and alloys with increasing strength has been a constant trigger for the technical development of our societies. Interestingly, nature does not use metals as structural materials at all. Practically all biological materials are based on polymers and polymer-mineral composites.

The required mechanical performance is obtained by an intelligent structure which is hierarchical and optimized at all levels [3]. **Figure 1** shows the hierarchical structure of spruce wood as an example. Annual rings with a thickness of a few millimeters are visible in the light-microscopic image of a cross-section (**Fig. 1a**). The structure at this level reveals a cellular material made of parallel tube-shaped cells, having a somewhat thicker cell-wall in latewood (LW) than in earlywood (EW). The cell wall itself is a fiber composite made of cellulose microfibrils embedded in a matrix of hemicelluloses and lignin. The cellulose microfibrils are helically wound around the axis of the wood cell with a diameter in the order of 20 micrometer (**Fig. 1b**). The cellulose fibrils, finally, contain cellulose nanocrystals (**Fig. 1c**). Studying the hierarchical structure of natural materials, such as wood [4], bone [12], tooth [14], collagen [11] is one of the research goals, aimed at linking the hierarchical structure to mechanical requirements of the tissue and, hence, extract some of the principles used by nature for mechanical optimization.

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Thesis: Investigation of an Al-Zn-Mg alloy using diffuse neutron scattering

**1981-1985:** Research Scientist (Austrian Academy of Sciences, Vienna; Laboratoire Leon Brillouin, Saclay, France);

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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)

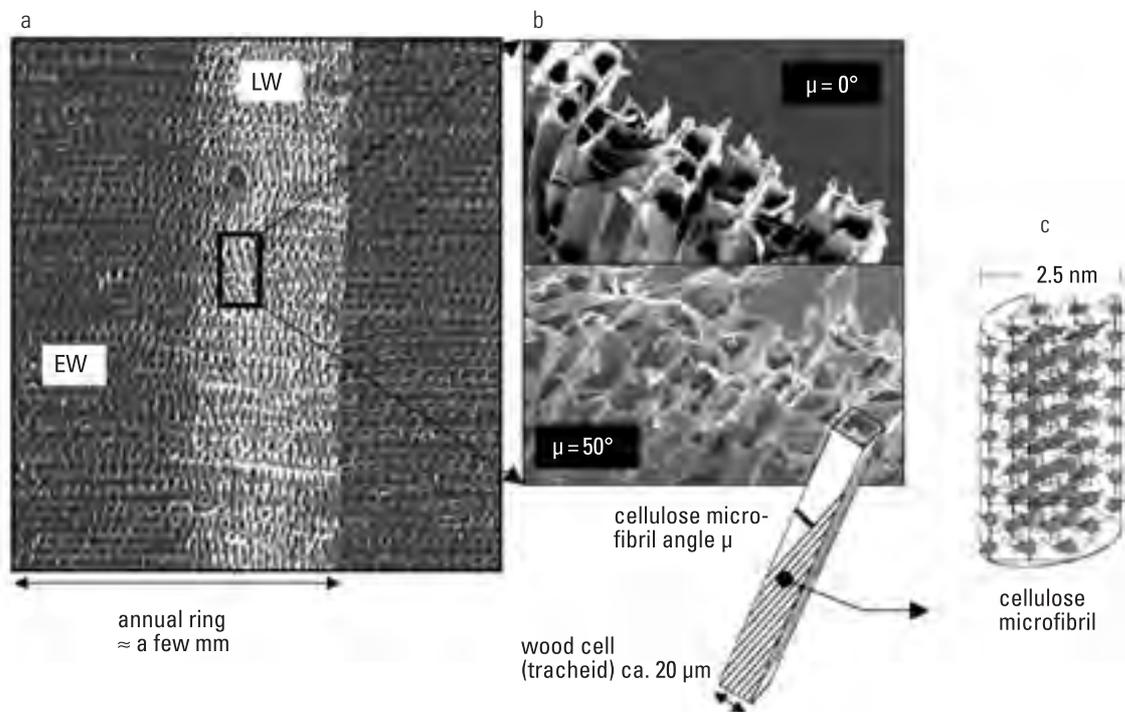
**1997:** Visiting Professor, (Physics Department of the University of Munich)

**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, Gölml)

Director (Erich Schmid Institute for Materials Science of the Austrian Academy of Sciences)



*Fig. 1: Hierarchical structure of wood. (a) Cross-section through the stem. Each annual ring is composed of earlywood (EW) and latewood (LW). (b) Fracture surfaces showing individual wood cells. The cell wall material is a composite of cellulose fibrils in a matrix of hemicelluloses and lignin.  $\mu$  is the spiral angle of the fibrils in the main cell wall layer. (c) Schematic representation of the crystalline structure of a typical cellulose fibril.*

## Biomimetic Materials

Some of the principles used by nature for mechanical optimization under the constraints imposed by the natural environment are tested for implementation in technical systems and materials. One of the methods used to explore these possibilities is rapid prototyping where extremely porous structures with designed geometry can be constructed out of virtually any material [13]. Porous scaffolds designed in hydroxyapatite (the bone mineral) with a strut thickness of a few hundred micrometers (Fig. 2) are currently tested in cell culture as a possible route for synthesizing bone replacement material. Research on biomimetic materials also includes the study of artificial collagen-mineral composites and metal nanoparticles synthesized in association with bacterial cell membranes.

## Biotemplating

A further approach towards the design of new materials based on natural models is biotemplating. This process consists of transforming the biological materials (e.g. wood) directly into technical structures by physical or chemical processing. The aim is to preserve as much as possible of the original hierarchical structure, copying it into a different material. Ongoing activities include studies on the carbonization of wood and the transformation into porous carbon-based ceramics. Indeed, it has been shown by different groups in recent years, that wood tissue can be transformed into cellular ceramics via a two step procedure: i) pyrolytic decomposition of wood, resulting in a porous carbon template, and ii) direct reaction to form carbide-ceramics, or infiltration of non reactive species for further processing to yield oxide-ceramics. The formation and the structure of the carbon template plays a key role in this context, since preferred



Fig. 2: Simple architecture made out of hydroxyapatite by rapid prototyping of the mould and subsequent gel casting (in collaboration with the Vienna University of Technology [13]). The strut thickness is close to the one of bone trabeculae (several hundred micrometers, see Fig. 3).

orientation and nano-porosity of the template may be controlled by the hierarchical structure of the original tissue and by the details of the conversion process. Current activities include studies on the chemical and structural development of wood during pyrolysis and on the microstructure and mechanical properties of the resulting carbon templates.

## Mechanical Adaptation of Biomaterials

It is well-known that biological materials constantly adapt to (even changing) mechanical needs. This is achieved by a strain-sensing mechanism, which in most biological systems is not fully elucidated. In the case of bone, for instance, some specialized cells (osteocytes) are thought to act as strain sensors and to be at the centre of a feed-back loop, called bone remodeling cycle, where damaged bone is removed and replaced by new material. This process is crucial for the tissue's capability of mechanical adaptation and self-repair. Some basic principles are currently studied by computer simulation. The mechanical optimization of natural composites, such as the mineralized collagen fibril, are studied by theoretical modeling [8] and by investigating experimentally the detailed response (both mechanical and biological) of the biological system to mechanical loads. Other examples of current interest are the deformation mechanism of tendons [11], of single wood fibers [1] or the structure development in systems with a defined load pattern, such as tree branches [2].

Tendons contain helically wound collagen molecules with a length of 300 nm and a thickness of about 1.5 nm. These molecules are assembled into fibrils which consist of staggered periodic arrays of these molecules. The fibrils are further assembled into fibres and finally into tendons. Structural changes during deformation of native tendons can be monitored "in-situ" by diffraction of synchrotron radiation while the tendon is being stretched. The x-ray diffraction yields the helix pitch of the molecules as well as the staggering period of the fibrils. Monitoring the changes in these parameters during stretching permits to measure the elongation of the molecules as well as the fibrils. It turns out that the molecules are extending less than the fibrils which are extending much less than the tendon as a whole. This means that not only the structure but also the deformation is hierarchical. This is possible because the various elements in the hierarchy can shear with respect to each other [11].

A similar approach is pursued for the analysis of the deformation of wood. In order to get a better understanding of how the elements in the hierarchy are optimized individually and contribute to the overall mechanical behavior of the tissue, methods have been developed to extract single native wood fibres without maceration or any other chemical treatment [1]. Such fibres have a thickness around 20 microns and can be individually analyzed by synchrotron radiation during deformation. Tree branches are particularly interesting to study mechanical adaptation since they have to grow horizontally and will experience predominantly tensile stresses on the upper side and compressive stresses on the lower side [2].

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### Bone Research and Medical Applications

The hierarchical structure of bone is schematically shown in Fig. 3. The interior of a human vertebra, for instance, is a cellular solid with struts of about 0.2 mm thickness. These struts are made of bone material which is a collagen matrix with lamellar organization and reinforced by calcium-phosphate nano-particles. Diseases may affect the bone structure at any of these levels and physical characterization helps elucidating how these diseases develop and how they contribute to fracture incidence, for example. Recent examples of studies with medical background relate to brittle bone disease [7], to hypophosphatasia [15], and to osteoporosis treatment with parathyroide hormone [9].

These studies have been carried out in close collaboration with the Ludwig Boltzmann Institute of Osteology in Vienna, Austria. In the first example, the aim was to elucidate the origin of the bone fragility in brittle bone disease, a rare congenital disease characterized primarily by a collagen defect. A combination of methods, including electron microscopy, x-ray scattering and mechanical testing has been employed to show that a weaker collagen matrix joined to over-mineralization might be at the origin of the fragility. Osteoporosis, on the other hand, is a widespread disease associated with low bone mass and increased fracture incidence. Osteoporosis treatments aim at increasing or stabilizing the bone mass. One of the important questions in this context is whether the various treatment strategies also affect the bone material quality. We have been addressing this question for different (potential) treatments including fluoride, bisphosphonates and, most recently, parathyroide hormone [9].

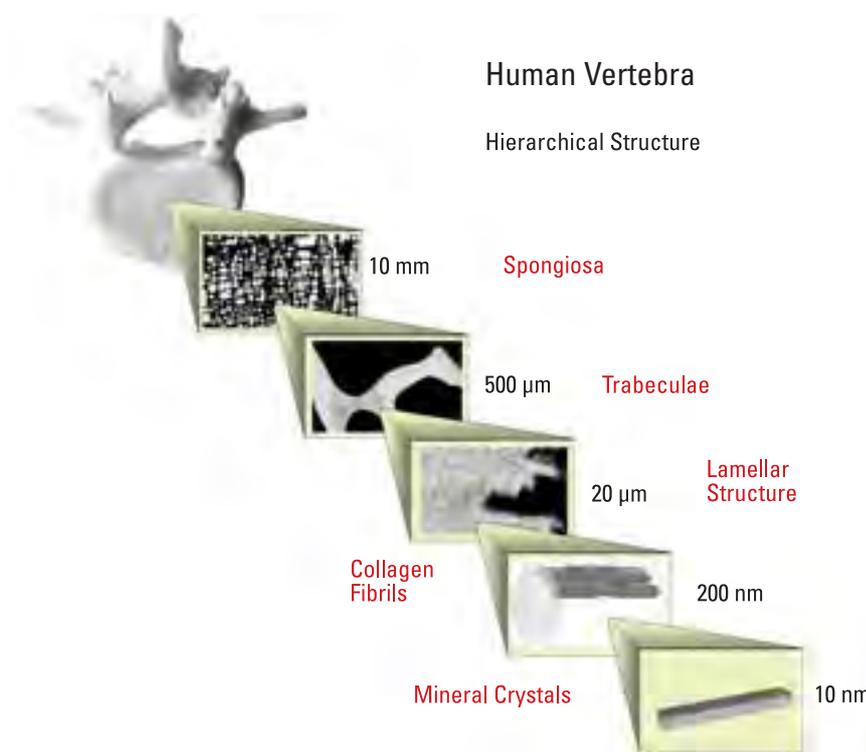


Fig. 3: Hierarchical structure of bone. The interior of a human vertebra is a spongy bone structure (spongiosa) with individual struts (trabeculae) having a thickness of about 0.2 mm. The bone material is a composite made of collagen fibrils reinforced with calcium phosphate nanoparticles. This fibre composite is assembled into a lamellar plywood-like structure. The mechanical properties depend on the detailed structure at each level of hierarchy. Similarly, diseases may affect any of these levels.

## New Methods for Materials Analysis

Most of the structural research mentioned previously requires state-of-the-art experimental equipment, but some needs the development of new approaches. Scanning methods based on the diffraction of synchrotron radiation [10], as well as the technique of small-angle x-ray scattering (SAXS) are continuously developed to improve the characterization of hierarchical biomaterials [5]. Fig. 4 shows the principles of scanning-SAXS, used to characterize bone on two hierarchical levels simultaneously. This approach can be used, e.g. to assess the effects of osteoporosis treatment on the quality of bone material [6]. Further technical improvement is expected from a dedicated scanning set-up which is planned to be installed at the synchrotron BESSY in Berlin.

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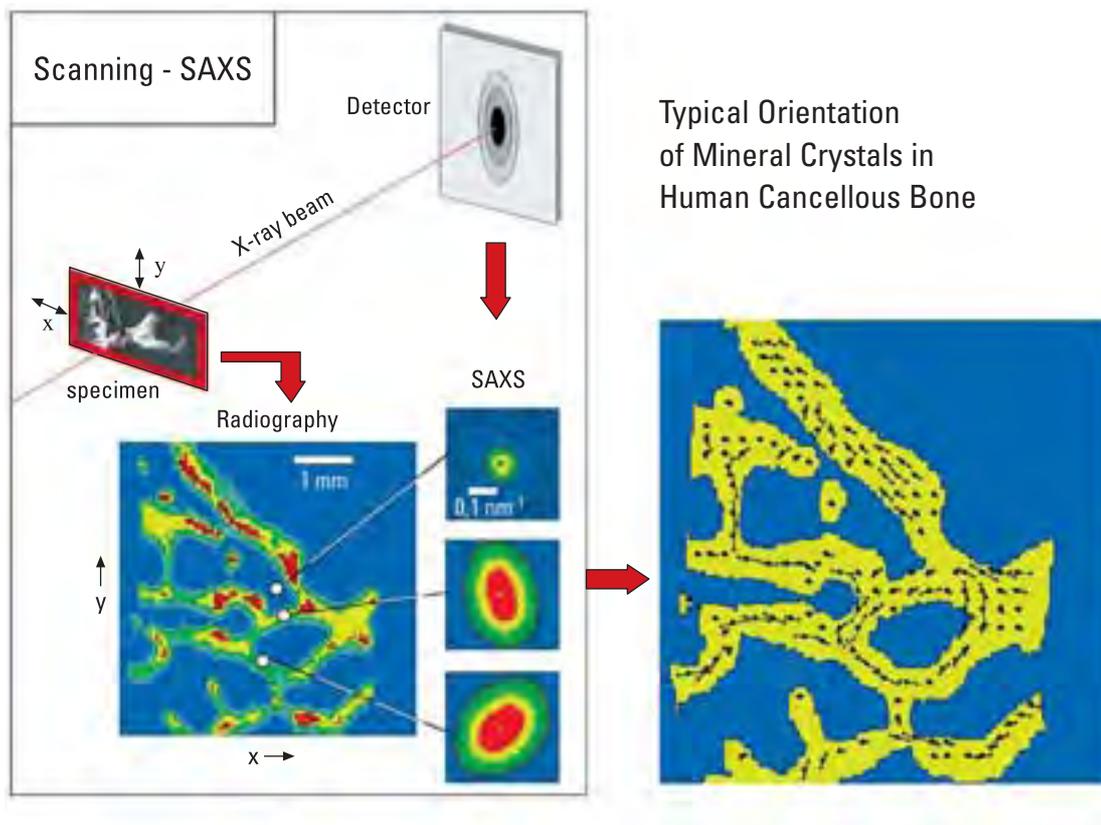


Fig. 4: The method of scanning small-angle x-ray scattering (scanning-SAXS) allows structure characterization at two hierarchical levels simultaneously. A narrow x-ray beam is scanned across the sample. This allows a resolution given by the size of the x-ray beam (typically in the order of micrometers). At each position, the evaluation of the SAXS-signal gives structural information at the nanometer level. The example shows the local orientation of plate-like mineral particles (represented by bars in the rightmost image) in a bone section.

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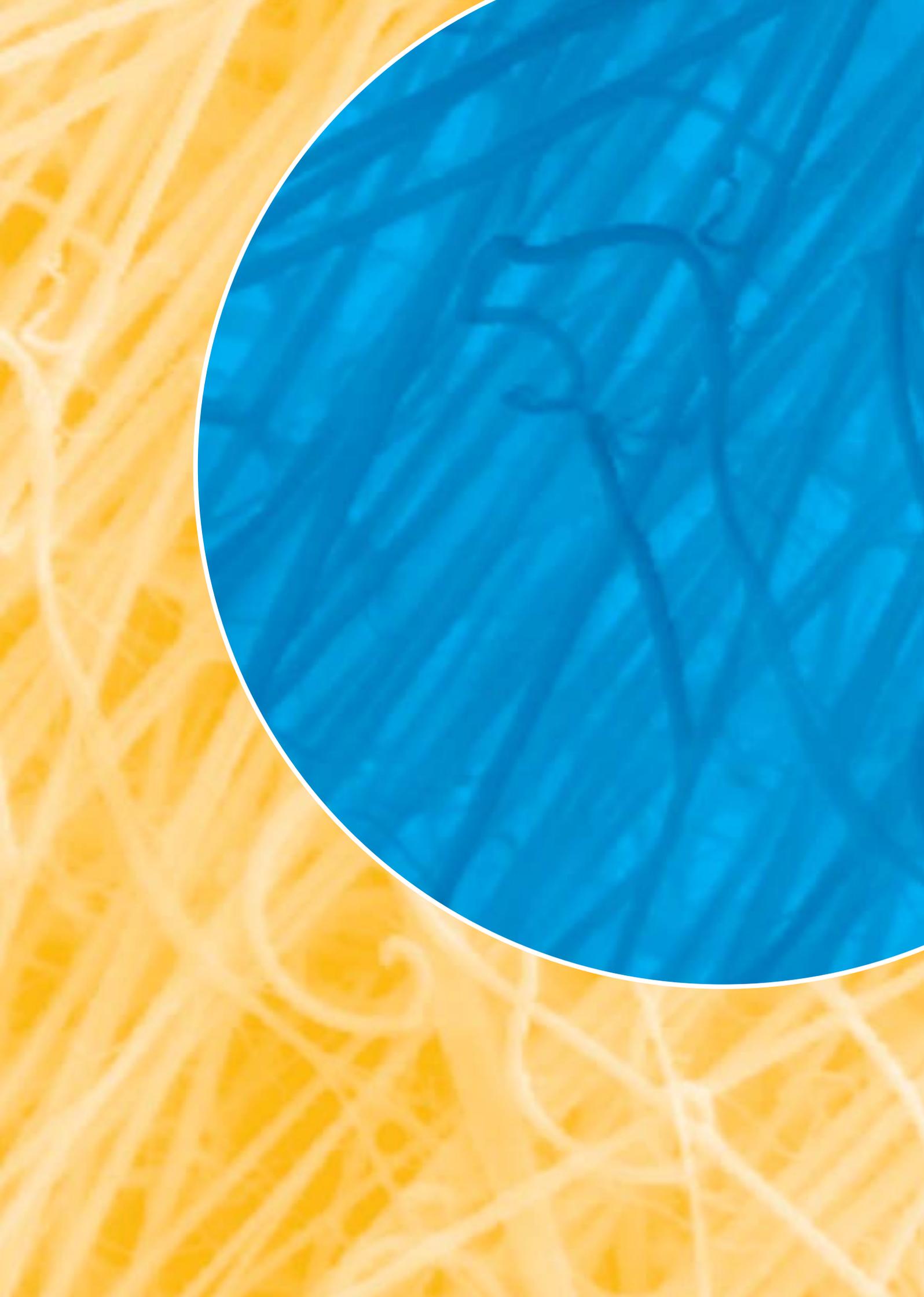
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**APPENDIX**

APPENDIX



# Organigramm

## Organization Chart

**Managing Director (2001-2002)**  
**Prof. Dr. Dr. h. c. Markus Antonietti**

**Department of Colloid Chemistry**  
 Director: Prof. Markus Antonietti · Secretary: Annette Page

**Heterophase Polymerization**

- Miniemulsions/[Dr. Katharina Landfester](#)
- Heterophase Polymerization/[Dr. Klaus Tauer](#)

**Polyelectrolytes and their Complexes**

- Ionic Self-Assembly: Facile Route for the Production of Functional Nanostructured Materials/[Dr. Charl F. J. Faul](#)

**Amphiphilic Polymers**

- Bioorganic -Synthetic Hybrid Polymers as Molecular LEGO<sup>®</sup>-Bricks/[Dr. Hans G. Börner](#)
- Biomimetic Mineralization/[Dr. Helmut Cölfen](#)
- Amphiphilic Block Copolymers/[Dr. Helmut Schlaad](#)

**Mesoporous Materials by Nanocasting and Nanocoating**

- Porous Materials via Nanocasting Procedures: Innovative Materials and learning about Softmatter Organization/[Prof. Markus Antonietti](#)
- Templating Strategies to Fabricate Controlled Morphology Networks/[Dr. Rachel A. Caruso](#)

**Modern Techniques of Colloid Analysis**

- Fractionating Colloid Analysis/[Dr. Helmut Cölfen](#)
- Electron Microscopic Studies of Colloidal Systems/[Dr. Jürgen Hartmann](#)
- Gel Permeation Chromatography (GPC), Static Light Scattering (SLS)/[Dr. Gudrun Rother](#)
- Modern Methods of Light Scattering/[Dr. Reinhard Sigel](#)

**Independent Research Group Surfactant Adsorption Layers**

- Adsorption Properties of Surfactants at Fluid and Solid Interfaces/[Dr. Klaus Lunkenheimer](#)

**Department of Interfaces**  
 Director: Prof. Helmuth Möhwald · Secretary: Karin Kreßler

**(Quasi) Planar Interfaces- Fluid Interfaces**

- Interactions in Complex Monolayers/[Dr. Gerald Brezesinski](#)
- Analysis – Synthesis – Purification of Amphiphiles /[Dr. Gunther Czichocki](#)
- Static and Dynamic Peculiarities of twodimensional Systems (Langmuir Monolayers)/[Dr. Thomas M. Fischer](#)
- Thermodynamics, Kinetics and Dilational Rheology of Interfacial Layers/[Dr. Reinhard Miller](#)
- Molecular Organization in Soluble Monolayers and Functional Films/[Dr. Hubert Motschmann](#)
- Thin Liquid Films/[Dr. Hans-Joachim Müller](#)
- Supramolecular Organization of Amphiphilic Monolayers/[Prof. Dieter Vollhardt](#)
- Rheological Properties of Fluid Interfaces/[Dr. Klaus-Dieter Wantke](#)

**Non-Planar Interfaces**

- Nanostructured Interfaces and Materials/[Prof. Frank Caruso](#)
- Mechanics and Adhesion of Capsules and Strongly Deformable Colloids/[Dr. Andreas Fery](#)
- Modular Materials: From Dynamic to Nanotechnological Devices/[Dr. Dirk G. Kurth](#)
- Bioinspired Control of Electrical and Optical Properties of Interfaces/[Prof. Helmuth Möhwald](#)
- Dynamics of Complex Polymer Layers/[Dr. Monika Schönhoff](#)
- Multifunctional Polymeric Micro- and Nanosized Capsules/[Dr. Gleb Sukhorukhov](#)

**Solid Interfaces**

- Nucleation, Interfacial Molecular Ordering and Wetting Behavior of Alkanes at Solid/Vapor Interfaces/[Dr. Hans Riegler](#)

**International Joint Laboratory**

- Assembly by Complex and Biomimetic Materials/[Prof. Junbai Li](#)

**Service NMR Spectroscopy**

[Dr. Monika Schönhoff](#)

## Department of Theory

Director: Prof. Reinhard Lipowsky - Secretary: Gudrun Conrad

- Wetting Phenomena at Structured Surfaces/Prof. Reinhard Lipowsky
- Wetting Transitions of Hydrocarbons on Water/Dr. Wilhelm Fenzl
- Mesoscopic Simulations of Biomimetic Membranes/Dr. Julian C. Shillcock
- Giant Vesicles – Helping us to Understand Biological Membranes/Dr. Rumiana Dimova
- New Membrane Physics with Polymersomes/Dr. Hans-Günther Döbereiner
- Emmy Noether Junior Research Group/Dr. Ulrich Schwarz
- Adhesion Behavior of Vesicles at Finite Temperature/Dr. Thomas Gruhn
- Membrane Adhesion/Dr. Thomas Weigl
- Protein Folding Kinetics/Dr. Thomas Weigl
- Polyelectrolytes/Dr. Christian Seidel
- Semiflexible Polymers and Filaments/Dr. Jan Kierfeld
- Molecular Motors and Active Systems/Prof. Reinhard Lipowsky
- Theoretical Evolutionary Ecology/Dr. Angelo Valleriani

### Administration/Other Services

Head: Reina Schlender - Secretary: Rita Heine

### Budgeting/Accountancy

Thea Dumke, Karin Schönfeld

### Personnel

Gisela Gutjahr, Gudrun Patz

### Procurement/Purchase

Sylvia Ost, Marianne Schulz

### Other Services

Peter Quasdorf, Bodo Ryschka

### IT-Service Group

Head: Dr. Ingolf Müller  
Thomas Baumann,  
Michael Born, Ingo Fiedler,  
Hans-Jürgen Schanze

### Library

Head: Dorothea Stscherbina  
Silke Niehaus-Weingärtner

### Drawing and Photography

Christine Steininger

### Public Relations

Katja Schulze

### Works Council

Peter Ebert

### Mechanic Workshop

Heads: Günter Haseloff,  
Wolfgang Katz  
Andreas Kretzschmar,  
Wolfgang Nierenz

### Electronic Workshop

Head: Peter Ebert  
Henryk Pitas, Monika Scholz,  
Wolfgang Stein

### Glass Blowing Workshop

Cliff Janiszewski

### Campus Technics

Head: Heiko Jung  
Hagen Hannemann, Dirk Nast,  
Heinz Schmidt, Thomas Vogt

### Caretaker

Peter Westermeier

# Fachbeirat

## Scientific Advisory Board

Name	Institution
Prof. Ruth Duncan	Welsh School of Pharmacy, Cardiff University
Prof. Gerhard D. Findenegg	Institut für Chemie, Technische Universität Berlin
Prof. Michael Grunze	Lehrstuhl für Angewandte Physikalische Chemie, Ruprecht-Karls-Universität Heidelberg
Dr. Rüdiger Iden	Polymer Physics, BASF Aktiengesellschaft
Prof. Michael Klein	Department of Chemistry, University of Pennsylvania/Philadelphia
Prof. Toyoki Kunitake	The University of Kitakyushu, RIKEN Institute
Prof. Dominique Langevin	Laboratoire de Physique des Solides UMR C8502, Université Paris Sud
Dr. Wolfgang von Rybinski	Henkel KGaA
Prof. Erich Sackmann	Physik Department E 22, Technische Universität München
Prof. Michael Schick	Department of Physics, University of Washington

# Drittmittelprojekte

## Third Party Funds

### BMBF

Zuwendungsgeber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
BMBF	Funktionale supramolekulare Systeme- Untersuchung von Wechselwirkungskräften und Adsorptionsverhalten bei Polyelektrolytmolekülen sowie deren Filmbildung auf molekularer Skala	Prof. Möhwald Dr. Akari GF	01.05.1999-31.12.2002	BASF AG Uni Greifswald
BMBF	Funktionale supramolekulare System-Herstellung, Charakterisierung und Nutzung von kompartimen- tierten dreidimensionalen Polyelektrolytnanofilmen mit kontrollierter Selbstassemblierung	Prof. Möhwald Dr. Donath GF	01.06.1999-31.08.2002	Uni Leipzig Institut f. Transfusions- medizin Berlin Microparticles GmbH Mediport Kardiotechnik GmbH Berlin
BMBF	BioFuture:Nanofabrikation neuartiger biofunk- tioneller Materialien und Bioverkapselung	Dr. F. Caruso GF	01.11.1999-31.10.2004	
BMBF	Polyoxometallate in maßgeschneiderten Amphiphilhüllen: Neuartige Wege zum selbst- organisierten Aufbau supramolekularer Funktionseinheiten	Dr. Kurth GF	01.04.2000-30.09.2001	Uni Bielefeld, Fakultät AC1
BMBF	Selbststrukturierende organisch-anorganische Hybridnanopartikel auf der Basis von amphiphilen Blockcopolymeren und Charakterisierung des Bildungsmechanismus ihrer Überstrukturen	Dr. Cölfen KC	01.04.2001-31.03.2004	Forschungszentrum Jülich GmbH
BMBF	Weiterentwicklung und Betrieb der Messstrecken A" und BW4 für Kleinwinkelstreuung am HASYLAB (DESY)	Dr. Fenzl GF/TH	01.04.2001-31.03.2004	
BMBF	Nanobiotechnologie-Verbundprojekt: Multifunktionale künstliche Zellen als Transporter, Sensoren und Nanoreaktoren	Dr. Sukhorukov GF	01.05.2002-30.04.2005	Uni Leipzig Capsolution Nanoscience AG
BMBF	Polymere Haftvermittler zur Verbesserung der Eigenschaften funktionaler Papiere	Dr. Riegler GF	01.04.2002-31.03.2005	SCA Hygiene Products GmbH Fraunhofer-Gesellschaft f. Angewandte Forschung e.V. Capsolution Nanoscience AG
DLR	Finanzierung der Reise- und Aufenthaltsausgaben für die Durchführung des "microgravity" Experiments- Reflight of FAST- im Rahmen der Shuttle Mission STS 107	Dr. Miller GF	01.09.2000-30.06.2003	
BMWi	INNOvationskompetenz mittelständischer Unternehmen: Ausarbeitung der konzeptionellen Idee und Testung der Entwicklungsstufen zur Entwicklung eines allgemein anwendbaren Gerätes zur Bestimmung der physiko-chemischen Stabilitätsparameter von Schaum...	Dr. Lunkenheimer UG	06.03.2002-30.06.2004	GIT Gesellschaft für innovative Technologie mbH
BAM(BMWi)	Nationale Tensid-Referenznormale	Dr. Lunkenheimer UG	01.11.2002-28.02.2003	

### Sonderforschungsbereiche (SFB 448)

Zuwendungsgeber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG/TU Bln.	Mesoskopisch strukturierte Verbundsysteme; Biomimetische Mineralisation mit amphiphilen Blockcopolymeren	Dr. Cölfen KC	01.01.1998-	
DFG/TU Bln.	Mesoskopisch strukturierte Verbundsysteme; Synthese und Untersuchung des Assoziationsverhaltens von neuen linearen und verzweigten amphiphilen Blockcopolymeren	Dr. Schlaad KC	01.01.1998-	
DFG/TU Bln.	Mesoskopisch strukturierte Verbundsysteme; Phasenverhalten reiner Stoffe und binärer Mischungen in geordneten mesoporösen Materialien	Prof. Antonietti KC	01.01.1998-	
DFG/TU Bln.	Mesoskopisch strukturierte Verbundsysteme; Wechselwirkung von Nanopartikeln und Membran	Prof. Lipowsky Dr. Döbereiner TH	01.01.1998-	
DFG/TU Bln.	Mesoskopisch strukturierte Verbundsysteme; Elektronentransferreaktionen in Materialien mit Polaritätsgradienten	Prof. Möhwald GF	01.01.1998-	Uni Potsdam
DFG/TU Bln.	Mesoskopisch strukturierte Verbundsysteme; Hierarchische Architekturen aus Modulen mit metallocupramolekularen Koordinations-Polyelektrolyten	Dr. Kurth GF	01.01.2001-	

### Industrie, nicht öffentliche Zuwendungsgeber

Roche (BMBF)	Herstellung und Charakterisierung von Hybrid-Nanopartikeln für bioanalytische Anwendungen	Prof. Antonietti Dr. Landfester KC	01.04.1999-31.03.2002	
Bayer AG	Untersuchung des Adsorptionsverhaltens von Dispergierhilfsmitteln auf Oberflächen von organischen Feststoffteilchen	Dr. Miller Dr. Lunkenheimer GF/UG	01.07.2000-30.06.2003	
Henkel KG	Delivery Systems-Untersuchung von Polymerisations- und Verkapselungsverfahren in Miniemulsion, Charakterisierung der Eigenschaften der enthaltenen Polymerpartikel	Prof. Antonietti KC	01.03.2000-01.03.2002	
BASF AG	Schaltbare Wirkstoff-Freisetzung durch Polyelektrolyt-Verkapselung	Dr. Donath GF	01.11.2000-30.09.2001	
BASF AG	Aufklärung von Reaktionsmechanismen bei Polymerisationsreaktionen	Prof. Antonietti KC	01.01.2000-31.12.2001	
BASF AG	Polyurethandispersionen via Mini-Emulsionspolymerisation	Dr. Landfester KC	1.12.2000-30.11.2003	
BASF AG	Entwicklung neuer Detektionstechniken für die Analytische Ultrazentrifugation	Dr. Cölfen KC	01.12.2001-30.11.2004	

## Industrie, nicht öffentliche Zuwendungsgeber

Zuwendungsgeber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
8sens.biognostic AG	Nanoverkapselte Enzymkristalle für Affinitätstests	Dr. F. Caruso GF	01.11.01-31.10.2003	
HMI Bln.GmbH	Wissenschaftliche und technische Zusammenarbeit auf dem Gebiet der Untersuchung von Oberflächen und dünnen Schichten mit Neutronenstreuung	Prof. Möhwald GF	01.01.1999-31.12.2004	
Mitsubishi	Surface control by functional polymers	Prof. Antonietti Dr. Landfester KC	01.03.2002-28.02.2003	
L'oreal	Nanocapsules and the encapsulation of lipophilic and hydrophilic molecules in particles composed of polyester ...	Prof. Antonietti KC	1.8.2002-31.07.2003	
AT&S	Kontrollierte Herstellung von Dispersionen leitfähiger Materialien	Prof. Antonietti Dr. Landfester KC	01.06.2002-31.05.2003	

## EU/ESA

EU	Structure, phase behaviour and properties of floating and transferred Langmuir monolayers and self-organized Multilayers of new mesophase silicon polymers	Prof. Möhwald GF	01.12.1998-30.11.2001	Riso National Laboratory, Roskilde State Scientific Center of Russia, Moskau Institute of Organoelement Compounds RAS, Moskau Institute of Physics, Kiev
EU	Nanocapsules with functionalized surfaces and walls	Prof. Möhwald GF	01.09.2000-31.08.2004	CNRS Toulouse EPFL - Dept. Chimie LCPPM, Lausanne ICFAM Genua Advanced Drug Delivery Technologies AG Muttentz Nimbus Biotechnologie GmbH Leipzig Faculdade Engenharia da Universidade do Porto, Porto Universität für Bodenkultur, Wien
EU	Polymerizable and polymeric surfactants in emulsion polymerization for water-borne coatings	Dr. Tauer KC	01.12.1997-28.02.2001	CNRS Villeurbanne Technische Universität Eindhoven Institute of Surface Chemistry AKCROS Chemicals AKZO-Nobel Resins AKZO-Nobel Coatings Vinamul, SCA GRAPHIC Reserche University of Riga

## EU/ESA

Zuwendungsgeber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
ESA/ESTEC	Topical Team: Progress in emulsion science and technology	Dr. Miller GF	01.03.2000-01.03.2002	Uni Aix-Marseille Uni Compiègne ICFAM Genua
ESA/ESTEC	FASES – Fundamental and applied studies of emulsion stability	Dr. Miller GF	01.10.2000-31.12.2002	ICFAM Genua Uni Florenz Uni Marseille Uni Compiègne ENITecnologie S. Donata Milanese

## Stiftungen

A.v.H.	Sofja Kovalevskaja Preis – Dr. Sukhorukov	Dr. Sukhorukov GF	01.12.2001-28.02.2005	
Zeitstiftung	Nanochemie für eine zukünftige Automobiltechnik	Prof. Antonietti KC	01.01.2001-31.12.2003	MPI Chemische Physik fester Stoffe MPI FHI MPI für Kohleforschung
VW-Stiftung	Tunable Selfassembled 2D and 3D photonic band-gap structures for applications in the visible optic, infrared and mm-wave ranges	Prof. Möhwald Dr. F. Caruso GF	01.03.2000-28.02.2003	Hebrew University of Jerusalem
VW-Stiftung	Polyoxometalate clusters in self-assembling hierarchical architectures: from discrete nanoscopic structures to extended liquid crystalline mesophases	Dr. Kurth	01.09.2002-31.08.2005	Uni Bielefeld Humboldt-Uni Berlin
VW-Stiftung	Biocomposite capsules as artificial viruses	Dr. Brezesinski GF	Beginn 01.03.2003	Uni Leipzig Uni Bochum

## DAAD

DAAD	Projektbezogener Personenaustausch mit Großbritannien	Dr. Kurth GF	01.07.2000-30.06.2002	
DAAD	Projektbezogener Personenaustausch mit Frankreich	Dr. Brezesinski GF	01.01.2001-31.12.2002	
DAAD	Projektbezogener Personenaustausch mit Hongkong	Dr. Caruso GF	01.01.2000-31.12.2001	
DAAD	Projektbezogener Personenaustausch mit Frankreich	Dr. Döbereiner TH	01.01.2001-31.12.2001	

**DFG**  
(ad personam)

Zuwendungs- geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Einfluss der Monoschichtstruktur einfacher und komplexer Phospholipidsysteme auf ihre Wechselwirkung mit Phospholipasen	Dr. Brezesinski GF	01.01.2000-31.12.2001	
DFG	Amyloidprotein-Lipid-Wechselwirkungen an Grenzflächen	Dr. Brezesinski GF	01.09.2000-31.08.2002	
DFG	Magnetische Eigenschaften, Strukturbildung und Synthese von Submikrometer magnetischen Hohlkugeln	Dr. F. Caruso GF	01.12.2001-31.05.2003	
DFG	Photonic Crystals from Coated Colloids	Dr. F. Caruso GF	01.08.2001-31.07.2003	
DFG	Kombination von Reflektions-Interferenz-Kontrast-Mikroskopie mit kraftmikroskopischen Methoden zur Untersuchung von Adhäsion und mechanischen Eigenschaften von Polyelektrolyt-Hohlkörpern	Dr. Fery GF		
DFG	Umorientierungsprozesse in hexatischen Langmuir-Monolayer-Phasen unter dem Einfluss lokaler Temperaturgradienten	Dr. Fischer GF	01.01.2000-31.12.2001	
DFG	Tripelpunktbenetzung in zweidimensionalen dipolaren Langmuir Filmen	Dr. Fischer GF	01.05.2000-31.08.2002	
DFG	Enzymatisch gesteuerte Benetzungsübergänge in zweidimensionalen dipolaren Langmuir-Filmen	Dr. Fischer GF	01.09.2002-31.08.2004	
DFG	Dünne metallosupramolekulare Polyelektrolytfilme	Dr. Kurth GF	01.09.2000-30.11.2002	
DFG	Untersuchung und Charakterisierung supramolekularer Aggregate	Dr. Kurth GF	01.12.2002-30.11.2004	
DFG	Oberflächenrheologische Charakterisierung von Schichten aus pulmonalen Surfactant bei Dilatation an Phasengrenzen zwischen einer wässrigen Lösung und unterschiedlichen Gasen	Dr. Miller GF	01.01.2000-31.12.2001	
DFG	Molekulare Orientierung und Aggregation von Tensiden an Grenzflächen zwischen zwei Flüssigkeiten	Dr. Miller GF	01.10.2001-30.09.2002	
DFG	Molekulare Orientierung und Aggregation von Tensiden an Grenzflächen zwischen zwei Flüssigkeiten	Dr. Miller GF	01.10.2002-30.09.2004	
DFG	Kopplung und Molekültransport an der Grenze Polyelektrolyt/Tensid	Prof. Möhwald GF	01.02.2000-31.07.2001	
DFG	Interactions of Bio-Polymers and Lipids in Layered Structures	Prof. Möhwald GF	01.08.2001-31.07.2003	

**DFG (ad personam)**

Zuwendungs- geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Interactions of Bio-Polymers and Lipids in Layered Structures	Prof. Möhwald GF	2001-2004	
DFG	Untersuchung der Gas-Permeation durch Schaumfilme	Dr. Müller GF	01.07.1999-31.08.2001	
DFG	Untersuchung der Gas-Permeation durch Schaumfilme	Dr. Müller GF	01.09.2001-31.08.2002	
DFG	Der Zusammenhang zwischen der Stabilität von Schäumen und Emulsionen und der Änderung der freien Energie bei der Bildung dünner Flüssigkeitsfilme	Dr. Müller GF	01.11.2000-31.05.2003	
DFG	Zusammenhang zwischen lokaler molekularer Ordnung an Grenzflächen und deren Benetzungsverhalten	Dr. Riegler GF	01.04.2000-31.03.2002	
DFG	Bildung zwei-dimensionaler hochorganisierter Strukturen auf Basis komplementärer Wasserstoffbrückenbindungen durch molekular-spezifische Erkennung	Prof. Vollhardt GF	26.11.2001-31.12.2003	
DFG	Auto-Oszillationen der Oberflächenspannung: Mechanismus und Wirkungsprinzipien eines neuartigen selbstorganisierenden dissipativen Systems	Prof. Vollhardt GF	15.05.2001-04.05.2003	
DFG	Der Einfluss molekularer Austauschvorgänge auf das rheologische Verhalten flüssiger Grenzflächen	Dr. Wantke GF	01.05.2000-30.04.2001	
DFG	Polyelektrolytkomplexe als Trägersysteme	Dr. Dautzenberg KC	01.04.2000-31.03.2002	
DFG	Controlled Radical Polymerization	Dr. Tauer KC	01.11.2002-31.10.2004	
DFG	Kolloidale magnetische Flüssigkeiten: Grundlagen, Entwicklung und Anwendung neuartiger Ferrofluide	Dr. Landfester KC	15.07.2000-14.07.2001	
DFG	Kolloidale magnetische Flüssigkeiten: Grundlagen, Entwicklung und Anwendung neuartiger Ferrofluide	Dr. Landfester KC	15.07.2001-26.04.2003	
DFG	Biokompatible magnetische Partikel: Herstellung und Charakterisierung polymerverkapselter, super-paramagnetischer Nanopartikel	Dr. Landfester KC	01.08.2002-	
DFG	Fluktuierende Riesenvesikel als morphologische Sonden zur Untersuchung der Materialeigenschaften amphiphiler Membranen und ihrer Wechselwirkung mit biologischen Makromolekülen	Dr. Döbereiner TH	01.05.2001-30.04.2003	

**DFG**  
(ad personam)

Zuwendungs- geber	Thema	Projektleiter	Bewilligungszeitraum	Zusammenarbeit mit
DFG	Benetzung und Strukturbildung an Grenzflächen	Prof. Lipowsky TH	01.10.1999-30.09.2001	
DFG	Be- und Entnetzung an lateral strukturierten Grenzflächen	Prof. Lipowsky TH	01.05.2001-30.06.2002	
DFG	Adhäsion von Vesikeln an lateral strukturierten Grenzflächen	Prof. Lipowsky TH	01.05.2002-30.04.2004	
DFG	Schwache und starke Polyelektrolyte an dielektrischen Grenzflächen	Dr. Netz TH	15.01.2001-14.01.2002	
DFG	Simulation von an einer Fest-Flüssig-Grenzfläche verankerten Polyelektrolytketten bei expliziter Behandlung von Gegen- und Salzionen	Dr. Seidel TH	01.08.2001-31.07.2003	
DFG	Emmy-Noether-Programm: Modelling forces and signalling in cell adhesion – Nachwuchsgruppe	Dr. U. Schwarz TH	01.11.2001-31.10.2003	
DFG	Emmy-Noether-Programm: Bioorganische und biometrische Polymere: Synthese, Charakterisierung und Anwendung der Polymerhybridsysteme – Nachwuchsgruppe	Dr. H. Börner KC	Beginn 02/2003	

# Wissenschaftliche Veranstaltungen

## Scientific Events

### Seminars

#### **Mineralisation Seminars**

- The Chemistry of Form, [Dr. H. Cölfen](#), MPIKG – 20.04.2001
- Nucleation Theory, [Dr. habil. K. Tauer](#), MPIKG - 04.05.2001
- Processing of Advanced Inorganic Nanomaterials, [S.-H. Yu](#), MPIKG - 18.05.2001
- Critical Crystal Nuclei, [G. Lucas](#), MPIKG - 13.07.2001
- Electrical Conductivity and Piezoelectricity in Iron Collagen Films, [V. Neto](#), MPIKG - 27.07.2001
- Dissipative Particle Dynamics, [Dr. J. Shillcock](#), MPIKG - 21.09.2001
- Electron Microscopic Characterization of Colloidal Crystals, [Dr. J. Hartmann](#), MPIKG - 05.10.2001
- Characterization of Minerals Using XRD Techniques, [B. Smarsly](#), MPIKG - 16.11.2001
- Biominerization, [P. Kasparova](#), 30.11.2001
- The Structure of Water, [Dr. Y. Mastai](#), MPIKG - 14.12.2001
- Atomic Force Microscopy, [Dr. A. Fery](#), MPIKG - 11.01.2002

#### **Membrane Seminar**

- Thermal Behavior of the Anionic Phospholipid DMPG, [Dr. K. Riske](#), MPIKG - 25.10.2001

### Colloquia:

#### **MPI Colloquia**

- Konjugierte Emitterstrukturen für organische elektronische Bauelemente, [Prof. U. Scherf](#), Universität Potsdam, Polymerchemie - 23.01.2001
- Thermodynamik und Kinetik der Wechselwirkung von Detergentien mit Membranen, [Prof. A. Blume](#), Phys. Chemie, Universität Halle - 06.02.2001
- Layered Structure of Liquids at the Solid-Liquid Interface, [Prof. H.-J. Butt](#), Universität Siegen - 24.04.2001
- Nanostrukturierte Hydrogele, ultradünne Filme und Nanoreaktoren aus amphiphilen Blockcopolymeren, [PD Dr. W. Meier](#), Universität Basel - 08.05.2001
- Formation and Reactivity of Metal and Semiconductor Nanoparticles in Silica Thin Films and Nanotubes, [Prof. M. Wark](#), Universität Bremen - 05.06.2001
- Using Heads as Feet to Walk Hand-over-Hand, Molecular Dynamics of the Kinesin Motor, [Prof. M. Schliwa](#), Universität München - 12.06.2001
- Annual Meeting Colloidal and Interfacial Science, [Researchers from the MPIKG and Alumnis](#) - 15.06.2001
- Kinetics of Surfactant Adsorption at Liquid Interfaces and their Dynamic Surface Tension, [Prof. D. Andelman](#), Tel Aviv University - 26.06.2001
- Inorganic Nanotubes and Inorganic Fullerene-like Materials from Layered Compounds", [Prof. R. Tenne](#), Weizmann Institute of Science, Rehovot, Israel - 24.07.2001
- Mesa Topography of Surfactant Monolayers, [Prof. T. Witten](#), University Chicago - 17.08.2001
- Polyelectrolyte Complexation and Multilayer Formation, [Prof. J.-F. Joanny](#), Institut Curie Paris - 11.09.2001
- Physics in Cell Biology: F-Actin as a Model System for Semiflexible Polymers", [Prof. E. Frey](#), Hahn-Meitner Institut, Berlin - 23.10.2001
- How Kinesin Couples ATP Hydrolysis to Motion along Microtubules: Theory and Experiment, [Prof. J. Howard](#), Max Planck Institute of Molecular Cell Biology and Genetics, Dresden - 04.12.2001
- Block Copolymer Surface Physics, [Prof. G. Krausch](#), Universität Bayreuth - 06.12.2001
- AFM-Force Spectroscopy: From the Manipulation of Single Polymer Chains to the Development of Nanoscopic Machines, [Dr. M. Seitz](#), Lehrstuhl für Angewandte Physik, LMU München - 12.12.2001
- Applied Biomimetics in Cooling Technology, [Dr. T. Zwiig](#), Danish Technology Institute and TU Dresden - 15.01.2002
- Polyelectrolyte Complexes: What Kind of Matter is that?, [Prof. M. A. Cohen Stuart](#), Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Netherlands - 05.02.2002
- Transport in Biological Systems", [Prof. A. Ott](#), Universität Bayreuth - 19.02.2002
- Production of Force and Movement by Polymerization of Actin: Mechanism and Reconstitution in Vitro, [Prof. M.-F. Carlier](#), CNRS Gif-sur-Yvette, France - 11.03.2002
- The Lego of Life: Microtubules as Dynamical Building Blocks of the Cytoskeleton", [Prof. B. Mulder](#), FOM Institute for Atomic and Molecular Physics, Amsterdam - 16.04.2002

- Cell Adhesion on Protein-Coated Micro-Patterned Substrates“, Prof. M. Bastmeyer, Universität Jena - 30.04.2002
- Dendrimer Controlled Crystallization Processes, Dr. N. A. J. M. Sommerdijk, Eindhoven University of Technology, Netherlands - 12.11.2002
- Industrielle Aspekte der Emulsionspolymerization, Dr. D. Distler, Abteilungsdirektor BASF AG – 26.11.200

#### **Colloquia SFB 448**

- Grosse Moleküle mit Funktion, S. Hecht, University of California at Berkeley - 17.04.2001
- Neue amphiphile Nanoobjekte: Janus-Micellen und Kern-Schale-Zylinder, Prof. A. Müller, Universität Bayreuth - 29.05.2001
- Nanoporoese Membranen durch Kolloid-Abformung, Dr. W. Goedel, Universität Ulm - 29.05.2001
- Controlled Synthesis of (Nano) Structured Materials, Dr. H. Börner, Carnegie Mellon University, Pittsburgh - 08.06.2001
- Characterization of Novel Materials and Nanostructures, Dr. J. Rice, CNRS, Orsay - 08.06.2001
- Modelling Relaxation Processes in Polyenes, Dr. C. Woywod, TU München - 08.06.2001
- Femtosekunden Ladungstransfer und Kontrolle der Adiabatzitaet in pyrenhaltigen substituierten Biphenylen, Dr. T. Fiebig, Universität München - 12.06.2001
- Self-Assembled Monolayers of Rigid Biphenyl Thiols: Structure and Applications, Prof. A. Ulman, Polytechnical University New York - 19.06.2001
- Mesostrukturierte Festkörper mit neuartigen Symmetrieeigenschaften, Dr. F. Marlow, MPI für Kohlenforschung, Mühlheim - 17.07.2001
- Polymere und Licht: Photonische Kristalle ausgehend von Polymeren, Prof. R. Zentel, Institut für Organische Chemie, Universität Mainz- 17.07.2001
- Mesoskopisch strukturierte Polymeroberflächen, Dr. P. Müller-Buschbaum, TU München - 29.01.2002
- Erzeugung von nanostrukturierten Oberflächen mit Polymeren, Prof. M. Stamm, Institut für Polymerforschung Dresden - 30.04.2002
- NMR-Untersuchungen von Gastmolekülen in mesoporoeseen Silikaten, Dr. habil. G. Buntkowsky, Insitut für Chemie, FU Berlin - 30.04.2002
- Komplexe Nanostrukturen in dünnen Blockcopolymerfilmen, Prof. G. Krausch, Universität Bayreuth - 28.05.2002
- Diblockcopolymer-Mesophasen durch Beta-Strukturierung und spezifische Wechselwirkungen, Dr. H. Schlaad, MPIKG - 28.05.2002
- Supramolecular Polymeric Architectures, Prof. E. W. Meijer, Eindhoven University, Netherlands - 18.06.2002
- Mehr-Schritt-Elektron-Transfer in Farbstoff-Dendrimer-Gerüsten, Prof. W. Rettig, HU Berlin - 29.10.2002
- Lokale Dynamik von Netzwerken und Grenzflächen in kolloidalen Systemen, Dr. T. Hellweg, TU Berlin - 29.10.2002
- Mesoskopisch strukturierte Farbstoff-, Farbstoff/Tensid- und Farbstoff/Polyelektrolyt-Aggregate, Dr. S. Kirstein, HU Berlin - 29.10.2002

#### **Biomimetic Colloquia**

- Opening Symposium IMPRS Biomimetic Systems, Prof. R. Lipowsky, Prof. F. Scheller, Prof. P. Janmey, Prof. A. Khokhlov, Prof. P. Fratzl, Prof. Z. Ou-Yang and Prof. S. Mann - 27.04.2001
- Lipid Rafts in Model and Biological Membranes“, Prof. K. Jacobson, University of North Carolina at Chapel Hill, Dept. of Cell Biology - 23.11.2001
- IMPRS Symposium on Biomimetic Systems – 14./15.10.2002

#### **Special Colloquia**

- Colloquium to the Birthday of Prof. G. Kretzschmar – 22.11.2002 in the Institute

#### **Workshops**

- Workshop der Kraftspektroskopie im pN Bereich mittels AFM.- 09.10.2002

# Wissenschaftliche Abschlüsse und Preise

## Degrees and Awards

### Department of Colloid Chemistry

#### *Diploma Theses*

Nozari, S.: Joint Nucleation of Organic/Inorganic Nanoparticles. Potsdam 2002.

#### *PhD Theses*

General, S.: Polyelektrolyt-Tensid-Komplexe – nanostrukturierte biomimetische Arzneistoffträger. Berlin 2001.

Kasparova, P.: Doppelhydrophile Blockcopolymerer als Mineralisationstemplate. Potsdam 2002.

Khrenov, V.: Anwendung der Heterophasen-Polymerisation und CeIV Chemie zur Synthese von Blockcopolymeren. Potsdam 2002.

Kukula, H.: Lineare und verzweigte Blockcopolymerer aus Polypeptiden und synthetischen Polymeren. Potsdam 2001.

Padtberg, K.: On-line Verfolgung von Nukleierungsprozessen. Potsdam 2002

Polarz, S.: Konzepte zur Nanochemie auf der Basis von porösen Materialien. Potsdam 2001.

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Landfester, K.: Miniemulsions for Polymerization Processes and Materials Science. Potsdam 2002.

#### *Awards*

Landfester, K.: Habilitandenpreis der Fachgruppe Makromolekulare Chemie der GdCh (2001)

Landfester, K.: Hermann Schnell Preis (2001)

## **Department of Interfaces**

### ***Diploma Theses***

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Schwarz, B.: NMR Spektroskopie an Polyelektrolyt Mono- und Multischicht-Systemen. Potsdam 2002

Steffen, P.: Rheologie und Benetzung in Langmir-Filmen auf Mikrometerskala. Potsdam 2001.

Teppner, R.: Adsorptionsschichten an fluiden Grenzflächen: Skalengesetze und Ionenverteilungen. Potsdam 2001.

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Caruso, F.: Federation Award (2001)

Möhwald, H.: Lectureship Award of the Japanese Colloid Society, Sendai (2002)

Möhwald, H.: Founder's Lecture, London (2002)

Möhwald, H.: Eli Burstein Lecture, Philadelphia (2002)

Sukhorukov, G.: Sofia Kovalevskaja Preis (2001)

## **Department of Theory**

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Vogel, M.: Röntgenbeugung an hochorientierten Phospholipidmembranen. Potsdam 2001.

Kunze, K. K.: Electrostatic Organization of DNA. Potsdam 2001.

Moreira, A. G.: Charged Systems in Bulk and at Interfaces. Potsdam 2001.

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Netz, R.: Karl-Scheel-Preis der Deutschen Physikalischen Gesellschaft zu Berlin (2001)

Schwarz, U.: Emmy-Noether-Preis der Deutschen Forschungsgemeinschaft (2001)

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### **Patents**

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