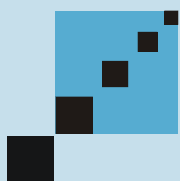
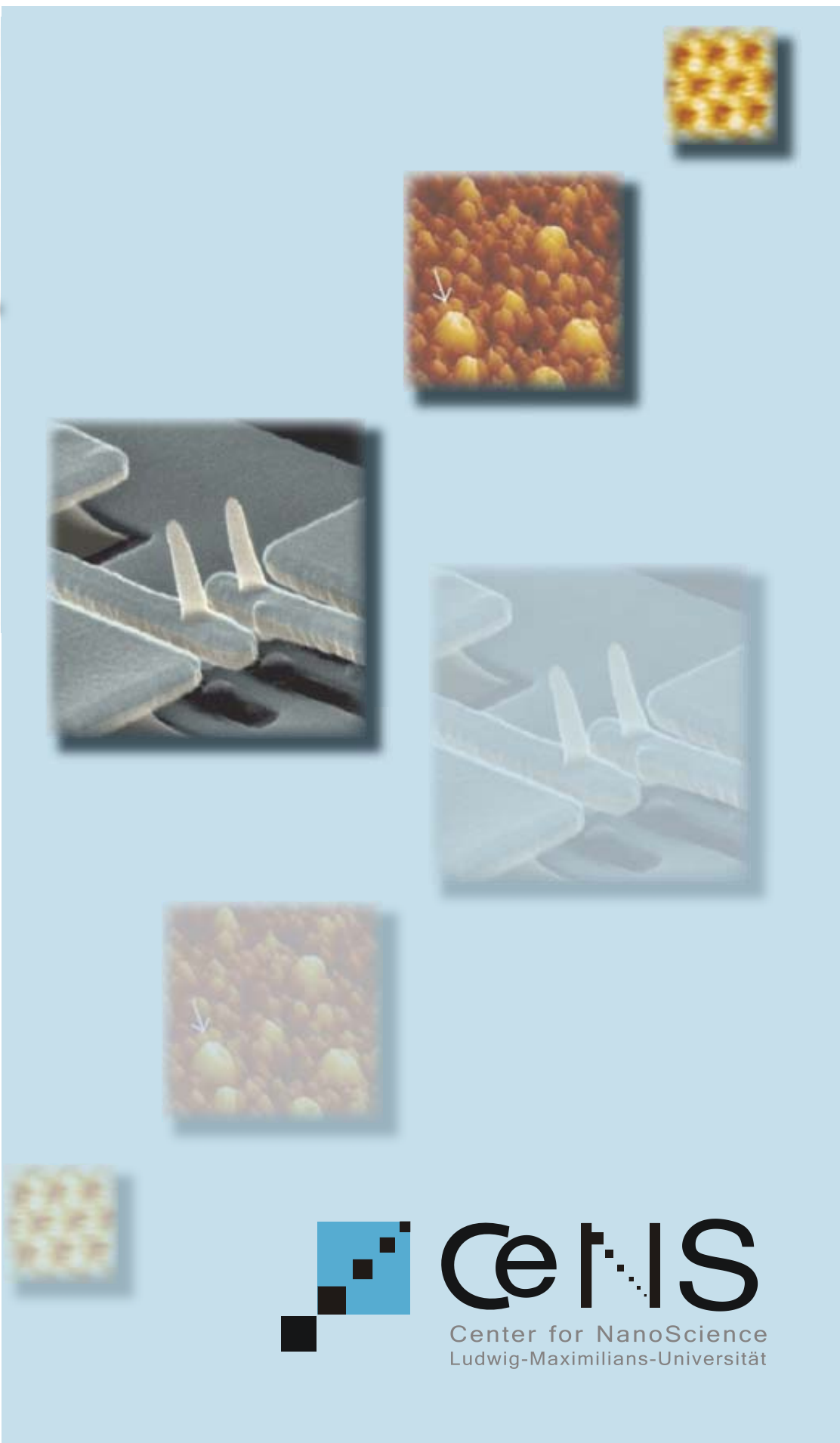


Annual Report 2002



CeMS

Center for NanoScience
Ludwig-Maximilians-Universität



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For further information about CeNS and the web-based version of this report please visit our website: www.cens.de

Introduction

In the year 2002, CeNS continued its success story and expanded with new members, stimulating educational activities and impressive science.

We are pleased to welcome Prof. Roland Netz, recently appointed as associate professor at the Sektion Physik of LMU, as full CeNS member. We are also happy to welcome our new extraordinary members, namely Prof. Peter Hänggi from our neighbor University of Augsburg, the LMU junior scientists Dr. Frank Wilhelm, Dr. Claus Duschl, Dr. Valentin Kahl, Dr. John Lupton, Dr. Wolfgang Parak, and Dr. Andrey Rogach as well as from the CeNS spin-off companies Dr. Hauke Clausen-Schaumann, Nanotype GmbH and Dr. Niels Fertig, Nan]i[on Technologies GmbH.

Junior members of CeNS have been offered attractive faculty positions elsewhere and have left or are in the process of leaving LMU to join other institutions but all plan to continue their collaboration within CeNS:

- Jan Behrends, as associate professor (C3) at University Freiburg
- Robert Blick, as associate professor at University of Wisconsin, Madison
- Uwe Klemradt, as associate professor (C3) at TH Aachen
- Klaus Meerholz, as full professor (C4) at University Köln
- Thomas Müller, as associate professor (C3) at University Heidelberg

Increased interdisciplinary research activities have been stimulated by the various CeNS workshops and seminars listed below, which hosted prominent guest speakers from all areas of NanoScience and introduced new students, postdocs and faculty members to the network of CeNS.

- "CeNS meets industry", June 21, 2002
- CeNS-Workshop „Membran-Biophysics“, July, 26-27, 2002
- CeNS-Workshop "Recent highlights in the Nanoworld", Wildbad Kreuth, October 6-9, 2002
- Biotech meets Nanotech 2002, organized by Bayern Innovativ, October 22, 2002
- The weekly seminar by CeNS

Major events were the Workshop at Wildbad Kreuth and the two bioscience-related workshops, all of them bringing together experienced researchers in key subjects of NanoScience and BioScience from all over the world with members and associates of CeNS. As previous workshops these recent activities also generated new interdisciplinary collaborations within CeNS and with other national and international partners.

In addition to the above mentioned workshops and the weekly "CeNS Oberseminar", jointly offered with the "Sektion Physik", with many highlight topics, a number of seminars with mostly international speakers were part of the weekly CeNS calendar (www.cens.de/calendar) and reflect the international interaction of CeNS. In addition CeNS hosted a large number of prominent guest researchers from all over the world who interacted fruitfully with CeNS members and students.

The successful interdisciplinary activities at CeNS are best demonstrated by the many master (30) and doctoral (16) thesis projects completed in 2002 as well as by the large number of publications in international journals of high visibility, many of which are coauthored by CeNS members belonging to different groups and disciplines as well as external partners. Consequently a large number of invited talks at conferences and workshops have been extended to CeNS members and associates and many of its scientific achievements have received special mention in the media. A significant number of joint publications can be traced to informal encounters between CeNS members at previous workshops.

At their yearly meeting, the CeNS members unanimously acclaimed the recommendation of the Advisory Board to continue the work of CeNS for the following five years. With completion of its second biannual term the members newly elected the CeNS Board now consisting of Christoph Bräuchle, Joachim Rädler and Jörg Kotthaus, who was again appointed spokesman of the board. The members also thanked Hermann Gaub for his strong engagement as a member of the previous board.

CeNS also hosted a number of visiting delegations e.g. from Japan and Singapore and single company representatives who were interested in learning about the wide science spectrum of CeNS as well as its unorthodox structures based solely on the voluntary engagement of CeNS members that make CeNS even for its founding members surprisingly successful.

The CeNS philosophy to operate as loosely organized working group stimulating the outreach across disciplinary and institutional boundaries now starts to become imitated elsewhere. Though initially surprising, the CeNS concept of avoiding an restricting institutional organization with centralized facilities, large staff and financial and academic power structures proves very successful as being solely based on voluntary activities it enables enormous flexibility and strengthens the role of junior scientists who are the spearhead of research and innovation. We thank our University and the State of Bavaria for supporting our initiative and hope they will continue to trust the CeNS concept, thus supporting the particular spirit and culture of CeNS that has found worldwide recognition.

Hoping that our friends and colleagues all over the world will enjoy the more detailed report below it is my pleasure to thank all CeNS members and associates for contributing to excellent science, promising technologies and valuable and joyful education.

Jörg P. Kotthaus
Spokesman of the board



CeNS members and associates at Wildbad Kreuth

Nano-Bio-Science

One of the major subjects worked on at CeNS have a biological origin, especially the research on DNA and on proteins. Modern biology provides stunningly clean and well-controlled samples making precise Physics experiments possible and allowing the design of new materials with novel properties. Further issues are molecular machines, research into the process of vision and the development of novel patch-clamp techniques integrated into a special chip.

The Atomic Force Microscope (AFM) is an instrument that works with an accuracy of a few Ångström under physiological conditions. It is ideal equipped for investigating functional bio-molecules. Especially with force spectroscopy, an AFM-based technique, the group of Hermann Gaub applies and detects pico Newton forces on single molecules. They investigate the mechanical properties of a molecule immobilized between the force sensor tip and the piezo-electric actuator of the AFM. A typical application is to let two individual bio-molecules interact with each other and separate them again. With this setup forces involved in molecular recognition (e.g. antibody – antigen) or in cell to cell adhesion directly are measured. Furthermore single molecule force spectroscopy reveals mechanical properties of individual bio-molecules by unzipping or unfolding them. One example for the many applications is scrutinizing the changes on the mechanical properties of DNA in the presence of anticancer drugs. (Rupert et al.). Most powerful is combining two modes of the AFM: high resolution imaging of a bio-membrane surface and force spectroscopy when unfolding a single molecule while lifting it out of this membrane. (Oesterhelt et al.) Theoretical analysis of the experiments and the resulting data is carried out in cooperation with the group of Roland Netz.

Fluorescence microscopy allows the direct observation of individual biological macromolecules. The Rädler group studies linear DNA molecules electrostatically adsorbed to cationic substrate-supported lipid bilayers. The DNA molecules are free to diffuse laterally but are restricted to the two-dimensional surface of the membrane. These strongly adsorbed, but laterally free DNA molecules provide comprehensive evidence for polymer statistics in two dimensions and have potential application for molecular analytics.

In the Simmel group, DNA is manipulated in microfabricated structures using electrical fields and microfluidics: The behavior of macromolecules in microfabricated structures is of great interest for many biomedical applications. Counting and sorting molecules, or control over biomolecular recognition events such as DNA hybridization are important tasks in biomedical analysis. On microfabricated chips these tasks might be performed more efficiently, cheaper and faster than in conventional analysis systems. In this context, the group investigate the behavior of

DNA molecules in static and varying electrical fields which are produced between microfabricated electrodes on a chip. DNA solutions are delivered to the electrodes in microfluidic channels fabricated by soft-lithographic methods. DNA motion is monitored using fluorescence microscopy.

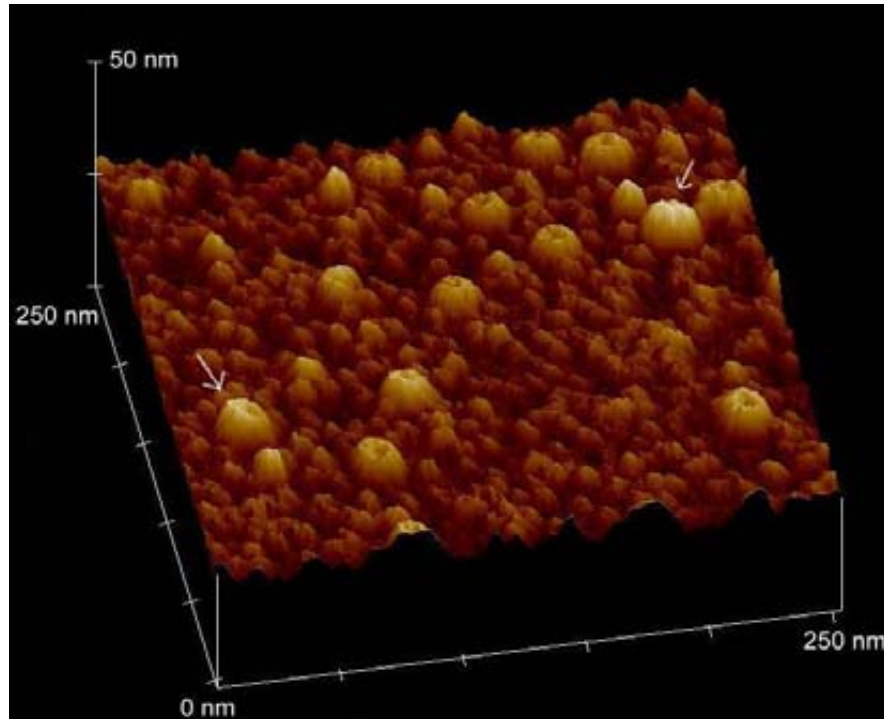
Another approach has been chosen by the group around Wolfgang Heckl and Stefan Thalhammer, in cooperation with Jörg Kotthaus and Bert Lorenz: They focus in their experiments on the non-contact and contact isolation of minimal amounts of genetic material from chromosomes for further biochemical diagnosis, using atomic force microscope (AFM) based nanomanipulation. The aim is to microdissect minute amount of genetic material of human metaphase chromosomes.

To increase the efficiency of the process, the extraction rate with the AFM tip is increased by the use of electron beam deposition. The adhering genetic material could be used for unspecific amplification. This was performed by modification of an adaptor-linked polymerase chain reaction (PCR) in cooperation with Achim Wixforth.

Non-contact isolation of genetic material was performed in the same group by using UV-A laser coupled into an inverted microscope. One field of interest is the isolation of single chloroplasts for taxonomy studies, single chromosomes for the generation of specific painting probes, hepatocytes for tissue transplantation.

Not only the properties of DNA are investigated at CeNS, also first experiments on the manipulation and self-organization properties are carried out in the group of Fritz Simmel in order to construct molecular devices. This is done utilizing the molecular recognition properties of DNA. The resulting devices can be cyclically switched between several conformations. Such simple switches might form the basis of more complex molecular machines which could be used for the directed assembly of nanostructures. The motion of these molecular devices is monitored using various fluorescence techniques.

The first step to the construction of a molecular motor in a nanomachine consists in the construction of a molecular rotor. Of special interest are light-driven molecular rotors since they may be easily controlled by the irradiation of light. However, while the concept is simple, its realisation is not straight-forward. The aim is to synthesise a molecular system that, upon irradiation with light, exhibits unidirectional rotation by 360 degrees or at least rotation preferentially in one direction. Recently, Feringa et al. published the successful synthesis of a light-driven unidirectional rotor. They are investigating this system with excited-state first-principles molecular dynamics using the ROKS approach in order to understand the mechanism theoretically. The theoretical studies



AFM-image of the ring-shaped chaperonin GroEL (SR1). GroEL is a protein complex which promotes folding of not correctly folded proteins. The arrows point to chaperonins. (J. Schiener, R. Guckenberger)

carried out in the group of Irmgard Frank shall help to design more efficient molecular rotors.

But not only DNA is in the focus of interest at CeNS. The folding and degradation properties of proteins are investigated in the group of Reinhard Guckenberger. Their main focus is on the function of macromolecular complexes which are involved in the folding and degradation of proteins. Proteins can only function correctly when they are in the correct folding state. Some proteins need the help of so called chaperonins to reach this state. Degradation of proteins is part of the functional cycle of cells (recycling of proteins) but is also important to remove incorrectly folded proteins (a kind of quality control).

The Guckenberger group concentrates on investigating the functional cycle of the chaperonin GroEL which is driven by ATP, for various protein substrates to be folded. For the first experiments they used a single ring mutant of GroEL and have seen conformational changes of the GroEL/substrate complex when adding ATP. Their second project is about the proteasome which is responsible for the degradation of incorrectly folded proteins. After investigation of preparation methods to achieve homogeneous samples with defined orientation of the proteasomes, they are now about to switch to functional studies.

A completely different subject is addressed in the group of Irmgard Frank: The details of the process of vision have been subject to

many theoretical and experimental studies but are still not well-understood. It takes place in the human eye and known has been so far that it is initiated by the absorption of a photon in the retina protein rhodopsin. Within 200 fs a certain double bond rotates by 180 degrees with a quantum yield of 67 percent.

After the construction of a theoretical model of this extremely efficient nanomachine (protein plus environment: 24000 atoms) and testing its stability with ground-state molecular dynamics, the group is now simulating the motion after transition to the first excited state. They employ restricted open-shell Kohn-Sham (ROKS) theory for the active part of the protein in combination with classical molecular dynamics for the rest of the system. This approach is on the one hand approximate enough to make the description of the dynamics of a system with several thousand atoms feasible. On the other hand, the quantum mechanical description of the active part is accurate enough to allow the simulation of chemical reactions.

A nanostructured chip for ion channels in cell membranes was developed in a collaboration between solid state physics (Robert Blick and Jörg Kotthaus) and Physiology (Jan Behrends): in the novel planar glass sensing chip a nanostructured aperture replicates the tip of a patch clamp pipette conventionally used for electrical recordings of current flow through cell membranes. This chip has several advantages over the classical pipette, including lower electrical noise and better accessibility of the membrane for concomitant use of nanotechniques such as AFM and single molecule fluorescence. In addition, the planar chip facilitates automation and parallelization of the patch clamp technique, which will be of great value in industrial drug screening. Strong cooperation took place in the project with Nanion Technologies, Andrew Woolley (Univ. Toronto), Gerhard Schütz (Univ. Linz) and Peter Hänggi.

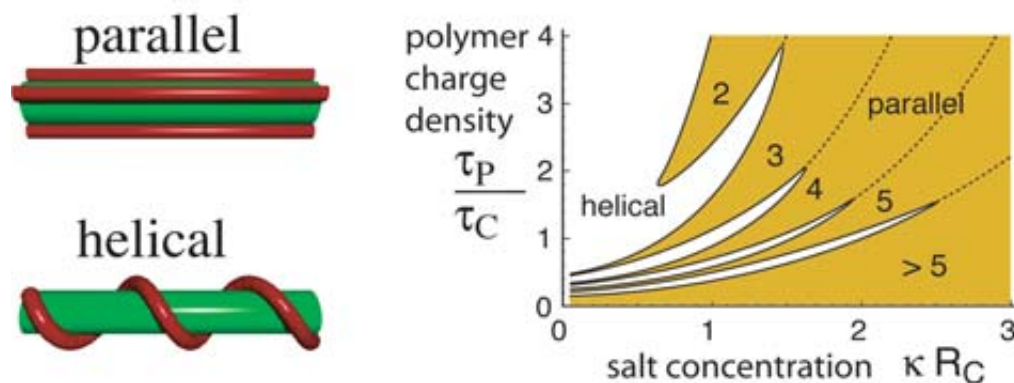
The interconnection between cells and semiconductors is investigated in the group of Hermann Gaub in cooperation with Jörg Kotthaus. These experiments provide new insights in cellular processes and neuronal networks. To deal with the complexity of neuronal networks complicated readout systems like the LAPS or the FAPS with high spatial resolution are necessary.

Physical Properties of Nanostructures

"Nanostructures" is a very flexible expression, ranging from biological molecules to semiconductor physics. CeNS members focus also on nanometer sized polymer properties.

When semiflexible charged polymers are mixed with much stiffer oppositely charged polymers, a complex forms where the more flexible polyelectrolyte (PE) wraps around the stiff polymer. Experimentally, such complexes itself fold up into toroidal or stem-like structures. This is an effect studied in the group of Roland Netz. In their theoretical research the group tries to understand the morphology of the underlying molecular complex, namely the conformation of the wrapping polymer: does it form a helix or does it adsorb in (one or more) parallel straight strands onto the cylinder? Using linear theory, transitions have been found between both morphologies as the salt concentration (or other parameters) are varied.

Most of the current interest in such complexes comes from their



The two possible complex morphologies and the phase diagram as a function of salt concentration and polymer charge density. (R. Netz)

potential applications in gene therapy (see the work by Joachim Rädler, the group's cooperation partner). The main problem here is to introduce genetic material into patients' cell nuclei, a process called DNA transfection. The results show that the morphology is dependent on the salt concentration, in qualitative agreement with experiments.

The Rädler group investigates the structure and properties of nanostructured biological materials and molecular layers at interfaces. Using synchrotron X-ray radiation the liquid crystalline structure and phase behavior of novel membrane/biopolymer composites is elucidated. In particular the condensed phases of DNA and oppositely charged lipids and polymers are of interest. These systems are used for gene

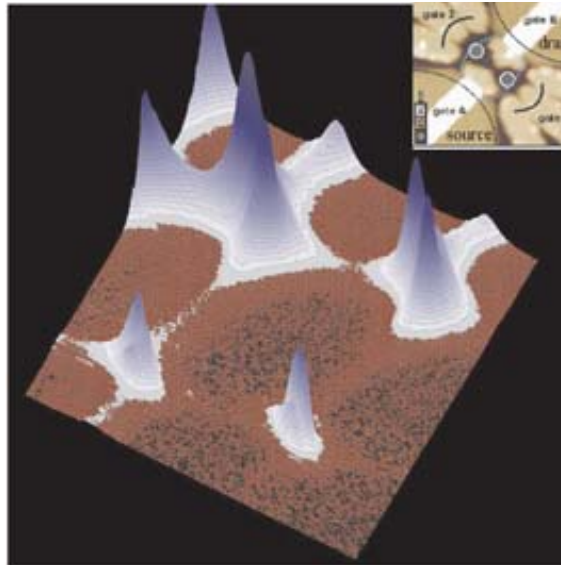
delivery and exhibit a regular layered architecture. The DNA phases consist of molecules with well defined electrostatic charges and theoretical models (as done by R. Netz) are able to predict structure and structural transitions.

In the group of Klaus Meerholz, organic electroluminescent diodes (OLEDs) are developed and characterized. The use especially for large area active flat-panel displays has become one of the target technologies for semiconducting conjugated oligomers and polymers. The group is working on the manipulation of the materials' work function, the fabrication of pixelated heterostructures by solution processing, and the realization of a polymeric injection laser.

The group of Jochen Feldmann and Uli Lemmer investigate the physical properties of OLEDs. Though conjugated polymers are already used in optoelectronic devices such as OLEDs and photodetectors, many microscopic processes leading to carrier relaxation and carrier transport are not yet understood. The group has experimentally addressed the issue of the generation scenario of charged carriers in organic photodiodes after photogeneration of hot excitons. By performing simultaneously optical pump and probe experiments as well as two-pulse photocurrent measurements the very different roles of excitons and polarons in the generation of charged carriers could be studied in detail. In addition, the optical gain induced by the high exciton density has been used to realize a novel polymer laser. In these organic lasers the distributed feedback is induced by a two-dimensional photonic crystal composed of gold nanoparticles. The nanoparticle array has been written by electron beam lithography on an ITO coated glass substrate. The realization of these novel organic lasers has been a joint collaboration with the group of Jörg Kotthaus.

The group around Jorg Kotthaus and Achim Wixforth studies the transient storage of optical information in GaAs-AlGaAs quantum wells employing superimposed voltage-tunable potential landscapes created either statically by electrodes or dynamically via surface acoustic waves. These potentials cause the reversible separation of electrons and holes created by interband absorption and thus can control the photoluminescence lifetime. The devices also allow to study the spatial spreading of unipolar charges via Maxwell relaxation. Many of these investigations are done in close cooperation with the theoretical group of Alexander Govorov in Novosibirsk.

A continuous fruitful collaboration also exists between the group of Jorg Kotthaus and the group of Valeri Dolgoplov at the Russian Academy of Sciences in Chernogolovka on studies of the phenomena related to the quantum Hall effect. In part this cooperation is supported by an Alexander von Humboldt award granted to Prof. Dolgoplov in 2002.



Two quantum dots are coupled in parallel via tunneling barriers. While first order tunneling can be suppressed, resonant co-tunneling of two electrons can be seen along lines in a typical phase diagram where an electron is delocalized over both dots (blue peaks)
 Inset: Atomic force micrograph of a real sample: The contact regions of both dots (dashed lines) are patterned with an additional dielectric spacer in order to provide the parallel access.
 (A. W. Holleitner)

Quantum dots are a further focal point investigated by CeNS members.

In the groups of Robert Blick and Jorg Kotthaus single electron transport is studied through very small Silicon quantum dots as well as single and coupled quantum dots defined by electrostatic potentials on GaAs-AlGaAs heterostructures. One highlight in 2002 was the observation of coherent electron transport through a quantum dot molecule (See Fig). Further details are found at <http://www.nano.physik.uni-muenchen.de> under Research/Report 2002.

The group of Jan von Delft uses theoretical approaches to the same systems. They have especially analyzed the suitability of coupled quantum dot systems for quantum computation and given design criteria for future experiments. They have also studied double quantum dot system with strong capacitive inter-dot coupling: The dots are attached to separate leads, and can be weakly coupled by tunnelling. They found that in the regime where there is a single electron on the two dots the low-energy behaviour is characterized by an $SU(4)$ -symmetric Fermi liquid theory with entangled spin and charge Kondo correlations. They have demonstrated that the application of a magnetic field gives rise to a large magnetoconductance. In a four-lead setup the double dot system can be used as a spin filter with perfectly spin-polarized transmission.

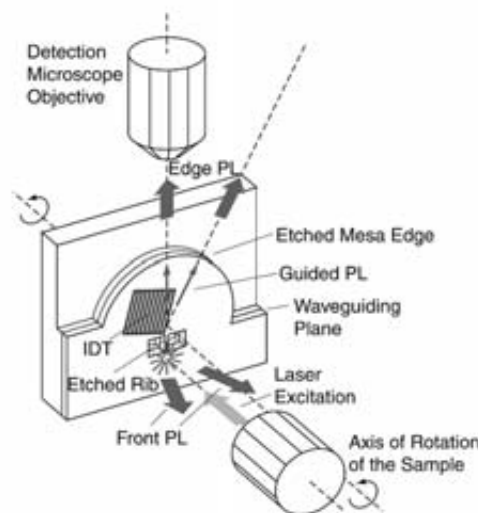
Furthermore, the group of Jan von Delft have developed a scheme for engineering decoherence in superconducting quantum bit circuits and have applied this to novel read-out schemes and quantum switches. They have demonstrated the feasibility of a 3-terminal nonequilibrium n -state in superconducting-normal hybrid devices and have quantitatively analyzed the performance of realistic, i.e. imperfect structures of that type. They have also studied the Josephson effect in coupled superconducting nanograins, and spindependent transport through ferromagnetic nanograins.

In the group of Khaled Karraï optical properties of single self-assembled quantum dots are investigated. The self-assembled InAs quantum dots are grown by molecular beam epitaxy in the group of Pierre Petroff in UC Santa Barbara. The quantum dots are bright emitter of light in the near infrared region (900 to 1200 nm). The emission line of a single dot can be made as small as few μeV at cryogenic temperatures which makes them also very suitable candidates for potential devices for quantum processing of information. Together with the group of Richard Warburton (Heriot Watt University Edinburgh) we have developed ways to fine tune the emission wavelength by Stark shift, Zeeman shift and diamagnetic shift. Also the number of electrons confined in the dots can be very conveniently adjusted one by one using a gate electrode. The charge tunable quantum dots are very suitable in order to investigate many body problems in a strongly confining potential. We have investigated such problems together with the theoretical input of Alexander Govorov. Optical properties of excitons in self-assembled quantum rings are also investigated. We predict that a neutral exciton (an electron and hole confined together in a quantum dot or ring) can exhibit quantum oscillations in the optical emission intensity as a function of magnetic field (Aharonov-Bohm oscillations). The oscillatory behavior is a function of the number flux quanta that can be threaded through the quantum ring. This effect is at first sight unexpected since such quantum oscillations are so far only known for charged particles.

Metal nanoparticles drastically change the fluorescent properties of dye molecules, an effect studied in the group of Jochen Feldmann. In most studied cases the molecular fluorescence is quenched, however, there are some reports on fluorescence enhancement effects near gold nanostructures. Various microscopic processes have to be considered in order to understand and predict the fluorescent properties of dye molecules near gold nanoparticles. These processes include Förster resonant energy transfer (FRET) and changes in the radiative rate due to dipole-dipole coupling effects. The group have carried out a systematic fluorescence study of lissamine molecules attached to differently sized gold nanoparticles. They find that the quenching efficiencies of the gold nanoparticles are extremely high compared to pure dye

systems. The analysis of time-resolved fluorescence data reveals that both the non-radiative and the radiative rates are changed when lissamine molecules emit in the vicinity of gold nanoparticles. These results show that even the smallest gold nanoparticles might be used as efficient acceptors in biophotonic FRET applications. The preparation part of this work has benefited from the intense interaction of graduate students from the groups of Prof. Gaub and Prof. Feldmann.

Optical wave-guides are central to the miniaturization of optoelectronic devices. Photonic structures are developed to bend the trajectory of light in such structures. However when such a photonic structure is fabricated its properties are hardly switchable or tunable. In the group of Khaled Karraï , Wolfgang Frank has designed and fabricated a functional electrically switchable in-plane Bragg reflector. The device can bend the trajectory of light just by applying a voltage on a metallic nanostructure patterned on a GaAs/AlGaAs planar wave guide (see figure)



Functional electrically switchable in-plane Bragg reflector. The device can bend the trajectory of light just by applying a voltage on a metallic nanostructure patterned on a GaAs/AlGaAs planar wave guide. (W. Frank, K. Karrai)

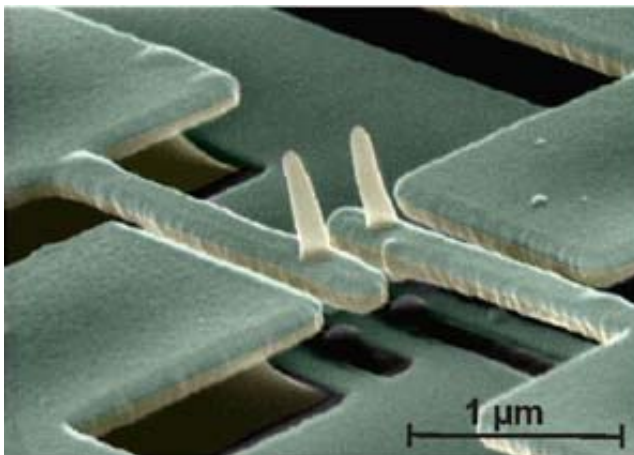
In the last decade the size of electromechanical systems was reduced from the microscale (MEMS) to the nanoscale (NEMS). The group of Willi Zwerger focus on the mechanical aspects of these systems and ask under which conditions quantum mechanical features arise and how they could be detected. They take mechanical resonators like microscopic beams as a model systems in order to investigate theoretically their properties.

Nanomechanical resonators are fabricated out of Silicon and GaAs in the group of Robert Blick and Jorg Kotthaus to study fundamental nanomechanical properties as well as the modified electron-phonon

interaction in such nanodevices. Possible applications range from environmental sensors and mechanical electron shuttles to ultrasensitive force and charge detectors.

Nanotweezers, the nanoscopic analogue of normal laboratory tweezers, could be very helpful tools for manipulating nanometer-sized objects. The group of Bert Lorenz use electron beam lithography and diverse etching techniques to fabricate the tweezers out of SOI material. Electron beam deposited tips are grown on top of the silicon prongs. Having built the nano-electromechanical structure, it is necessary to prove its functionality. For this purpose, an optical method was investigated. Images of the tweezers structures were taken by scanning confocal microscopy while the prongs were electrostatically deflected under a low frequency ac voltage. The images clearly resolve the actuating parts of the tweezers.

Focused-electron-beam-deposited carbon atomic-force microscope tips were characterized in the group of Bert Lorenz, together with Patrick Hoffmanni using flexural vibrations excited with piezoelectric transducers and observed directly inside a scanning electron microscope. Frequencies in the high-MHz range were measured and the elastic modulus was estimated to be 0.54 ± 0.16 TPa which is very close to the elastic modulus of nanotubes of about 1 TPa.



NanoTweezers:

You can recognize two silicon cantilevers with two diamond like isolating tips at the end. By applying a voltage between the two conductive silicon cantilevers the tips are moved towards each other like in closing tweezers. For more informations, please visit: <http://www2.nano.physik.uni-muenchen.de/~meyer/SFB486TPA2>

(C. Meyer, B. Lorenz)

Chemical Assembly of Nanostructures

One of the intriguing hopes in nano-bio medicine is to design molecular carriers that are able to efficiently deliver genetic material like plasmid DNA, antisense DNA or interfering RNA as therapeutic agents. A rational design of synthetic gene transfer vehicles aims at mimicking natural viruses using self-organized DNA/lipid/polypeptide aggregates. These so-called artificial or synthetic viruses are nanoparticles that carry a therapeutic plasmid DNA and the necessary biochemical derivatives for cell specific targeting and enhanced transfer efficiency. This venture requires a general understanding of self-organization of biological macromolecules such as DNA/lipid/polypeptide aggregates. Focus of the project is to establish a hierarchy of interfacial energies, which allows to build cascaded or multi-layered particles and to find mechanisms that preserve monodispersity of such systems. Once the desired nano-shuttles are developed the transport efficiencies in complex environments have to be measured. The Rädler group uses fluorescence correlation spectroscopy to follow the dynamics of macromolecules and colloids. Complementary the Bräuchle group, in collaboration, follows particles using the "virus tracing technique".

Another interest of the Rädler group is to build biologically programmable networks. Here novel organic-inorganic hybrid molecules are used to construct DNA based links and networks in aqueous and non-aqueous solutions. This approach might be valuable for efforts in electronic nano-bio-technology as carried out by F. Simmel.

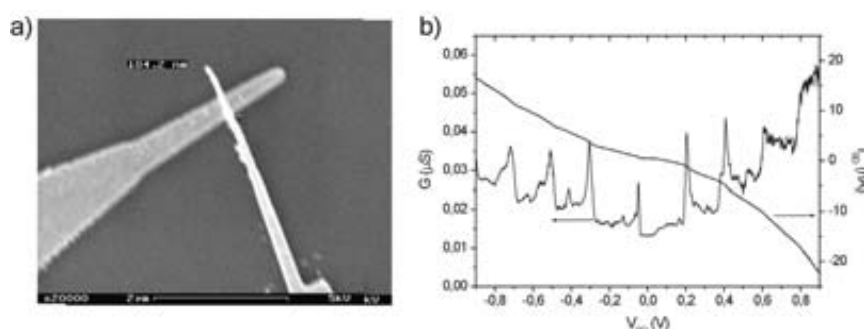
DNA can be used to build complex supramolecular structures which can serve as a template for the deposition or placement of nanoparticles and molecules. In a project in the group of Fritz Simmel, such DNA templates are used for the fabrication of electrical networks in a size range not accessible by conventional lithography. For electrical characterization, inorganically modified DNA networks are interfaced with lithographically defined micro- and nanostructures. Apart from the fabrication of nanoelectronic circuits, such DNA/inorganic hybrid structures may find application in the field of biosensors and actuators. This work was carried out in cooperation with Joachim Rädler and Wolfgang Parak.

Electronic transport through single carbon nanotubes and self-assembled monolayers of phenylene-based conjugated molecules was studied in the group of Udo Beierlein and Jörg Kotthaus. Carbon nanotubes were electrically contacted using electron beam lithography, followed by chemical wet etching in order to remove the substrate. These suspended nanotubes were then characterised in low temperature conductance measurements. Self-assembled monolayers of conjugated molecules were contacted

using two different approaches. Conductance measurements at low temperature show discrete structures for both types of devices which are interpreted as arising from quantum transport through molecular ensembles. Some of the molecules studied were synthesized in Ulrich Schubert's group at Eindhoven.

Nanolithography and the controlled build-up of small but controlled structures are important techniques in nanotechnology. There is at present an enormous drive in science towards the development of routes for the minituralization of devices with novel applications, e.g. high-density data storage and biological detector arrays. The group of Ulrich Schubert utilize scanning probe techniques for the fabrication of nanometer-sized structures on octadecyltrichlorosilane (OTS) passivated silicon wafers. By applying a bias voltage on a conductive AFM-tip the OTS layer on the surface can be oxidized very locally. The oxidation changes the local properties of the surface, thus opening routes to controlled surface modification via both absorption as well as chemical modification routes. This was shown in first exemplary experiments.

Scanning tunneling microscopy has also been used in the same group (Ulrich Schubert) to study the adsorbed phases of functionalized terpyridines at the solid-liquid interface of highly ordered pyrolytic graphite (HOPG). Terpyridines are well-known for their complexing behavior to transition metal ions making them widely used ligands in organometallic and supramolecular chemistry. They found that solutions of 2,2':6',2''-terpyridine-4'-oxy-dodecane (tpy-O-C12) and 2,2':6',2''-4'-oxy-octadecane (tpy-O-C18) form highly ordered 2D-arrays on HOPG in phenyloctane. For both compounds large well-defined lamellar domains have been observed with domain sizes larger than 500 nm. Sequential scans of an area with two-grain boundaries indicate that desorption/resorption is taking place along the domain edges. High-resolution images of the lamella have been obtained and the 2D packing within the lamella was determined in detail. The specific affinity of bipyridine and terpyridine ligands



- a) Crossed gold-contacts used for conductance measurements of self-assembled monolayers
- b) Conductance and current versus source-drain voltage of a self-assembled monolayer of 1,4 phenylenediisocyanide at 4.2 K. (U. Beierlein)

for transition metal complexes was also utilized in this group as new “smart” connection point between molecules, polymers and nano-objects. Besides functionalized fullerene units, conducting moieties or protein recognition groups and the self-organization of nano-particles was studied in cooperation with Jochen Feldmann. Very recently, the method was used in order to assemble macromolecules: Suitable functionalized polymers (decorated with terpyridine units) were combined to block copolymers and other architectures. The stepwise construction of the central terpyridine metal complexes can also be utilized on the nanoscale (see earlier experiments with H.E. Gaub utilizing modified AFM tips).

AFM experiments on polymeric systems are also carried out in the group of Hermann Gaub: There, the coupling of optical excitation into AFM-based force spectroscopy was developed. This allowed the scientists to investigate the transduction of optical excitation energy into mechanical force at the single molecule level, a central issue in the realization of man-made nanoscopic machines. Individual chains of a synthetic photochromic polymer containing the bistable photosensitive azobenzene moiety were found to lengthen and to contract by reversible optical switching of the azo groups between their trans and cis configurations. Upon photo-induced contraction against an external force acting along the polymer backbone, the polymer delivered mechanical work. Its operation in a periodic mode demonstrated for the first time opto-mechanical energy conversion in an artificial single molecule device.

In this group, the AFM technique is further applied to investigate the desorption (de-adhesion) of single polymer chains from physisorbed interfacial films on solid substrates such as metals and inorganic minerals. With the latest developments, it has now become possible to deposit single polymers at a certain position onto a bare solid surface, to let it adsorb, to pull it off the surface again, and to measure the forces involved in adsorption and desorption cycles with high precision and under equilibrium conditions. Hereby, the stable covalent attachment of a single or a small number of polymer molecules to an AFM cantilever tip has established individual polymer molecules as an interfacial analytical probe for the identification and measurement of various types of polymer-surface interactions.

For the use of gallium arsenide in future biosensors, ultrathin surface coatings are needed which provide a biocompatible interface for the cultivation of electrically active cells, and at the same time conserve the electronic characteristics of the semiconductor device under physiologically relevant conditions. Organosilicate-coatings were developed in the Gaub group with a thickness of 10-20 nanometers which allowed for the cultivation of NRK fibroblasts, chicken cardiomyocytes and nerve cells on gallium

arsenide substrates for a period of several days to weeks, at the same time conserving the electronic characteristics of GaAs-based FET test heterostructures.

The group of Thomas Bein develops assembly and patterning strategies for porous materials on planar surfaces for applications in selective chemical sensors; this is relevant for several transduction mechanisms such as acoustic waves on piezoelectric crystals, microcalorimetric detection (on special silicon chips or with infrared imaging), and optical changes in zeolite-encapsulated solvatochromic molecules. Assembly techniques range from oriented zeolite crystallization on self-assembled monolayers to the electrostatic assembly of pre-formed nanoscale zeolite crystals. Patterning techniques for array sensors are also being developed. A collaboration with the groups of Jörg Kotthaus and Achim Wixforth has been started in this area. Structural studies of these films using synchrotron radiation are being pursued in collaboration with Hartmut Metzger, a former CeNS member, at ILL at Grenoble.

In the group of Andreas Zumbusch, it has been demonstrated that it is possible to detect, characterize and follow the behavior of single molecules incorporated into the nanometer sized structures of molecular sieves. With this possibility a new wealth of information can be obtained for these so-called host-guest materials: The orientational distribution of molecules as well as the dynamic spectral, orientational and translational behavior of individual molecules. In this field the cooperation with the group of Thomas Bein shows a high potential. It has been possible to characterize the diffusion of guest molecules in different molecular sieves synthesized by that group.

The Bein group also explore different means of structuring very thin films with accessible channel systems that can serve as hosts for the oriented growth of ordered patterns of conducting and semi-conducting materials. This work builds on their previous efforts directed towards the encapsulation of conducting polymers, carbon, and charge-transfer salts in the nanometer channels of mesoporous hosts. The resulting conducting nanostructures in thin film host systems will be investigated in collaboration with CeNS colleagues in Physics, by using, for example, scanning probe microscopies or lithographically defined testbeds.

Another focus of the Bein group is on the synthesis of porous materials. The research concentrates on chemistry and function in designed nanoscopic spaces such as zeolites and periodic mesoporous hosts. The nucleation and crystallization mechanisms of nanoscale porous crystals as well as the role of molecular templates for the growth of novel zeolite structures are being investigated. In the field of zeolite synthesis, they develop

automated, parallel methodologies that allow to access a range of synthetic parameters vastly greater than the range possible with manual techniques, for the synthesis of known and new materials, including aluminosilicates, aluminophosphates, and titanosilicates.

In the subject of host-guest catalyst systems, the group of Thomas Bein works on modifying porous hosts by immobilizing or grafting selective molecular catalysts (such as transition metal complexes) into the interior of their channel systems, thereby creating highly selective heterogeneous catalysts. Presently, they are developing synthetic strategies to achieve control over the site density, orientation, and molecular environment of the catalyst (such as a porphyrin) in the cages and channels, including periodic mesoporous systems.

In another project, the group of Thomas Müller focus on the synthetic access to three-dimensional nanometersized conjugated molecules with tetrahedral symmetry. The electronic properties in the ensemble reveal a significant electronic coupling between the four electrophor branches. A perspective of these novel molecules is the use in OLED or OFET as tetrafunctional emitter, electron or hole transport layers. The group now plan self assembly and possible nanostructuration of these 2-4 nm sized molecular entities.

The Müller group also research in the field of the synthetic access to oligophenothiazines with nanometersized dimension. Electronically, these redox active oligomers display a strong electronic coupling as shown by cyclic voltammetry in the ensemble. First measurements of the current-voltage behavior in a hole-only OLED reveals that this class of materials is an excellent hole conductor. Alkynylbridged systems were self assembled on HOPG and display for the pattern a significant dependence on the N-alkyl substitution. Synthetically, they could broaden the scope to electronically modified derivatives that now allow to fine-tune important molecular electronic properties such as oxidation potential, absorption or emission. In addition, they have been successful in synthesizing and characterizing the ensemble properties of thiol ester terminated alkynylated (oligo)phenothiazines that now can be characterized in their single molecule behavior. Future plans for using oligophenothiazines as hole transport layers in OLED and OFET are still under investigation. The detailed characterization of self-assembly and nanostructuration will be also pursued.

Analytical and Imaging Methods

Single Virus Tracing is a microscopic technique, which was developed in the group of Christoph Bräuchle and allows the real time tracking of the infectious entry pathway of single viruses in living cells. This can be done with a high spatial accuracy (40 nm) and time resolution (10 ms). The dye labeling of the viruses can be reduced to only one dye molecule per virus in order not to disturb the virus-cell interactions. For the first time the mechanistic course of events during the entry of the viruses into a cell such as membrane penetration, diffusion, active transport in cytoplasm or penetration of the nuclear envelope can be visualized live and in detail. (Science, 294 (2001) 1929).

Recently this group has applied this novel method to single HIV-particles. Virions have been labeled with GFP in the gag protein. Special goals are a detailed understanding of the interactions leading to fusion of the HIV with the cell membrane (entry of the virus into the cell plasma) and the visualization of the effects of antiviral drugs, which prevent this step. This will help to develop efficient antiviral drugs.

A further research subject of the group of Christoph Bräuchle is the study of the dynamics of single molecules in nanostructured porous materials like molecular sieves. Such systems are very significant for many industrial processes like separation of molecules, shape selective catalysis and others. In all these processes the motion of molecules in the nanosized channels of these materials plays the central role. However, so far only ensembles of molecules could be observed. Using single molecule detection techniques, we were able to study the dynamics of individual molecules for the first time. This opens up the door to a new wealth of information on such host-guest systems (C. Seebacher et al., J.Phys.Chem.B. 106 (2002) 5591). In this field the cooperation with the group of Thomas Bein, who is synthesizing different types of molecular sieves, shows great potential.

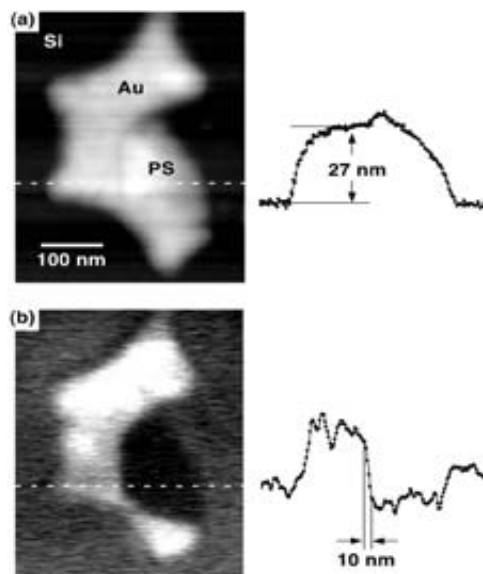
Phycocyanin (PEC) is the short wavelength absorbing pigment in the light harvesting complex of cyanobacteria. The group of Andreas Zumbusch performed single molecule investigations of PEC at room temperature as well as at cryogenic temperatures in order to gain a better understanding of the energy transfer processes in PEC. In a collaboration with the group of Hugo Scheer (Botanisches Institut, LMU Munich) they were able to investigate the different subunits separately and study the influence of aggregation of the different subunits constituting the native trimeric and hexameric form of the protein. Results from experiments employing polarization sensitive and spectrally selective excitation and emission detection show a wealth of different behaviours unobservable with common bulk techniques.

Using sensors based on the surface plasmon resonance (SPR) and combining it with a laser cavity, the group of Klaus Meerholz was able to increase the sensitivity by several orders of magnitude. They are currently modelling the devices and studying model reactions (e.g. adsorption of thiols on gold). They plan to apply these biochips for high-throughput (HTS) applications.

Another project in this group aims at the development of multiple-video-rate holographic imaging for medical purposes, e.g. for dermatology.

The group of Andreas Zumbusch developed a novel microscopic technique with contrast generation based on Coherent Anti-Stokes Raman Scattering (CARS). Here, the resonant excitation of molecular vibrations is exploited for selective imaging and the necessity for sample staining is removed. Other than IR microscopy and conventional Raman microscopy, CARS microscopy offers high sensitivity with a three dimensional spatial resolution similar to common two photon microscopy. The necessary excitation intensities are very low and make live cell imaging of prokaryotic and eukaryotic cells possible. Recently, the group has extended the technique to CARS correlation spectroscopy. In this case, CARS signal fluctuations caused by the diffusion of small particles through a fixed focal volume are recorded. CARS correlation spectroscopy has the promise to yield new insights in to aggregation phenomena of proteins which are of importance in a wide variety of diseases.

The group of Fritz Keilmann uses optical near-field microscopy techniques to investigate plasmon-resonant nanoparticles, thus understanding better the near-field interaction. They were able to predict and verify how to suppress background scattering, hitherto a serious obstacle against s-SNOM use now overcome (patent pending). As the theory quantitatively predicts s-SNOM contrast,



Optical contrast at 10nm resolution. The sample is a crescent-shaped Au island engulfing a polystyrene (PS) particle on Si. The optical near-field image (b) exhibits a strong contrast between Au and PS, so it can sharply detect the material boundary which on the other hand is not even visible in the simultaneously taken AFM topography (a). (F. Keilmann)

it was possible to establish a categorical sequence of near-field brightness that increases from dielectrics to semiconductors to metals. As the microscope also works in the mid-infrared, it is possible to discover the phenomenon of phonon-polariton-induced near-field resonance. Interesting applications are foreseen for discriminating between chemical or crystallographic subphases in nanocomposite material, and solve interesting questions, for example, of biomineralisation or extraterrestrial materials.

SNOM experiments are also carried out in the group of Reinhard Guckenberger, but in fluorescence mode. Fluorescence allows easy identification of labelled spots of biological specimens. Compared to the confocal laser scanning microscope, SNOM achieves a higher resolution and allows to acquire a topographical signal simultaneously with the optical signal which facilitates interpretation of the images. To minimize bleaching of fluorophores, the aperture SNOM is best choice, but the scattering SNOM achieves higher resolution. The group combined the advantages of the both types of SNOM by producing a metal tip on the aperture of a conventional fiber tip. With this new kind of probe they achieved in fluorescence a resolution of about 20 nm and were able to image single fluorophores. The first step of the production of the extra metal tip is to grow an electron beam deposited (EBD) tip which was done in collaboration with the group of Bert Lorenz. The EBD tip consists mainly of carbon and is finally coated with metal.

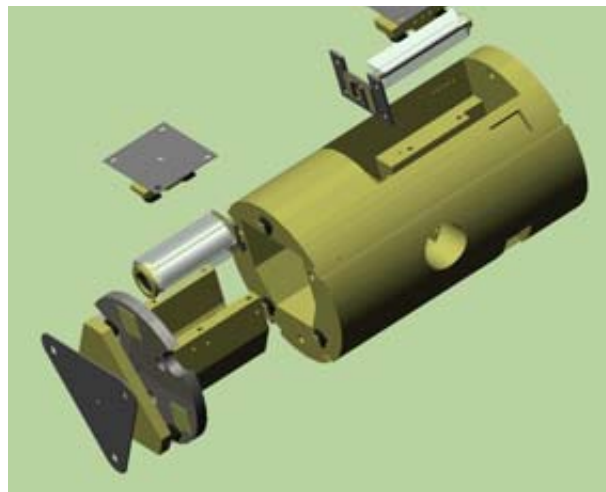
In the drive towards single molecule manipulation, combined techniques such as atomic force spectroscopy and optical fluorescence microscopy can achieve more than the sum of their parts. Atomic force spectroscopy offers the unique possibility to study the mechanics of polymer molecules on a single molecule level, thus circumventing ensemble-averaging effects. The usefulness of this method has been demonstrated in the group of Andreas Zumbusch in studies of many biologically significant molecules such as DNA and sugars or on organic polymers. On the other hand, optical detection provides an intriguing method to resolve the position of said molecules. By examining the fluorescence of intercalating dyes and simultaneously stretching single DNA strands with an AFM tip, new insights into the interaction mechanics of these dyes with DNA can be gained. Furthermore, the real-time observation and manipulation of relevant single polymers, such as DNA promises to open up a whole host of new possibilities, with far reaching consequences in the field of nano-technology.

AFM work was also done in the Guckenberger group, devoted to a better understanding of the tapping mode. For tapping in air, they found that measurement of higher eigenmode oscillations allows to analyze the tip-sample interaction in time. Generalizing this approach they even succeeded in measuring for the first time the forces acting on the AFM tip during tapping quantitatively and time-resolved.

This work was supported by a collaboration with the group of Wolfgang Heckl who did model calculations.

The groups of Khaled Karrai and Michael Reichling combine their complementary expertises in low temperature and highest resolution scanning probe techniques to set up a low temperature force microscope operated in the ultra-high vacuum. It is planned to use the instrument for atomic resolution studies on insulators, molecules and molecular films on dielectric substrates, the ultra-high sensitivity detection of nanoscale charge patterns and work function differences as well as fundamental studies on atomic scale friction and energy dissipation phenomena in tip-sample interaction.

The system is also prepared for an applied project investigating the friction and sliding properties of nanopositioning systems. The instrument is a home built microscope based on the designs developed by the Wiesendanger (Hamburg) and Güntherodt (Basel) groups. It consists of a scan head (see picture), integrating the sample stage and scanner, the cantilever assembly, and an optical fiber positioner for the interferometric detection system. The scan head will be operated in an ultra-high vacuum IHe bath cryostat. In 2002 the parts for the scan head have been designed and machined and are currently assembled.



Schematic image of the scan head for the low temperature force microscope operated in the ultra-high vacuum. (K. Karrai, M. Reichling)

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Bein

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Gaub

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Michael Breit

Nonlinear optical investigations of metallic nanostructures

Niels Fertig

Development of a Biochip for Electrophysiological Investigation of Ion Channels

Dirk Haft

Optische Spektroskopie an einzelnen InGaAs-Quanteninseln

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Untersuchung zum Antigen-Bindungsverhalten an einzelnen biologischen Nanoassemblies über den Energietransfer nach Förster

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Photonische Speicherzellen in lateralen Potentialübergittern

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DNA Einzelmolekülmechanik

Christoph Lingk

Ultrafast dynamics in quantum dots and quantum dot lasers

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Erhöhung der Sensitivität photorefraktiver holographischer Speichermedien auf der Basis von amorphen organischen Materialien

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High throughput methods in the discovery and application of nanoporous materials

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Aufbau und Charakterisierung eines konfokalen Tieftemperaturmikroskops und Spektroskopie einzelner organischer Moleküle in mesoporösen Wirtssystemen

Christian Seebacher
Einzelmolekülspektroskopie von organischen Farbstoffmolekülen in porösen Festkörpern und Tieftemperaturspektroskopie an dem grün fluoreszierenden Protein

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Tetraarylmethane mit chromo- und elektrophoren Gruppen - Synthese und intramolekulare elektronische Kommunikation von tetraedrisch arrangierten π -Systemen

Diploma theses

Stephan Angloher
Synthesis, characterization and application of bio-organic complexes on mesoporous support systems

Alex Darga
Lithographic methods for structuring mesoporous thin films

Christian Dupraz
Elektrischer Transport durch molekulare Systeme

Rachid Fetouaki
Immobilisation of transition metal-containing complexes of the porphyrin type in mesoporous materials MCM-41 and MCM-48

Stefan Fischerländer
Einzelmolekülkraftspektroskopie an DNA

Thomas Franzl
Development of a highly sensitive immunoassay

Sebastian Gritschneider
Atomare Kontraste in der dynamischen Kraftmikroskopie auf Fluoriden und Calcit

Udo Hartmann
Theory for Quantum Dot Charge qubits – Decoherence due to cotunneling

Alexander Högele
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Jochen Kirschbaum
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Johanna Kirstein
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Stefan Kowarik
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Robert Köppe
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Thomas Krämer
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Eveline Lancon
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Sina Lohmann
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Susanne Maier
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Stephan Malkmus
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Thomas Niedereichholz
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Hubertus von Poschinger-Camphausen
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Sebastian Rhode
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Martin Rotter
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Alexander Schiller
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Florian Schindler
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Florian Schrank
High-frequency Spectroscopy on Ion Channels in Cell Membranes

Constanze Sobotta
Stochastic Resonance of Alamethicin Channels in Bilipid-Membranes

Markus Storz
Decoherence of coupled solid-state qubits

Dorothee Wasserberg
Synthesis and investigation of photoactive metallo-supramolecular fullerene assemblies

Jan Weber
Tunneldynamik von Quantenpunkten in externen Feldern

Zulassungsarbeiten

Ingrid van Baal
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Richard Schloderer
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Awards

Prof. Christoph Bräuchle

- Karl Heinz Beckurts-Preis 2002

Prof. Wolfgang M. Heckl

- Communicator Prize of German Research Society

PD Dr. Klaus Meerholz

- Erich-Schott award 2002

- Visiting professor, Université Luis Pasteur, Strasbourg/France

Dr. Friedrich Simmel

- Emmy-Noether-Stipendium der DFG

Funding

BASF <http://www.basf.de>

Bavarian California Technology Center (BaCaTech) www.bacatec.de

Bavarian-French University-Center <http://www.ccufb.uni-muenchen.de/accueil.html>

Bayerische Forschungsstiftung <http://www.forschungsstiftung.de/>

Bayerisches Materialforschungsprogramm

BMBF - Bundesministerium für Bildung und Forschung <http://www.bmbf.de/>

Centre Nationale de la recherche scientifique CNRS <http://www.cnrs.fr/>

DFG Schwerpunktprogramm: Halbleiter und Metallcluster <http://www.dfg.de>

DFG-Sonderforschungsbereiche SFB 455; SFB 486; SFB 533; SFB 563 <http://www.dfg.de>

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European Union: Information Society Technologies Initiative: Quiprocone Network (travel grant) <http://www.quiprocone.org/funding.htm>

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German Academic Exchange Service (DAAD): DAAD / NSF travel grant <http://www.daad.de/>

Spintronics Research Training Network of the European Commission

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Verband Deutscher Ingenieure VDI <http://www.vdi.de/>

Volkswagen-Stiftung <http://www.volkswagen-stiftung.de/>

Joint Projects for Education and Training

- "CeNS meets industry", 21 June 2002
- Workshop „Membranbiophysics“, 26/27 July 2002
- Workshop "Recent highlights in the Nanoworld", Wildbad Kreuth, 6-9 October 2002
- Biotech meets Nanotech 2002, 22 October 2002
- The weekly seminar by CeNS

