

FOM 01.0270
March 2001

ANNUAL REPORT 2000

visitors guide
2001



FOM Institute for Atomic and Molecular Physics (AMOLF)

Kruislaan 407
1098 SJ Amsterdam
The Netherlands
Phone: +31 20 608 1234
Fax: +31 20 668 4106
E-mail: secr@amolf.nl
URL: www.amolf.nl

CONTENTS

INTRODUCTION	page 6
PART I	13
1. QUANTUM DYNAMICS OF ATOMIC AND MOLECULAR SYSTEMS	14
1.1 Vibrational dynamics	16
1.2 Extreme ultraviolet physics	18
1.3 Atoms in strong radiation	20
1.4 Femto-physics	22
1.5 Atmospheric photophysics	24
2. MASS SPECTROMETRY OF MACROMOLECULAR SYSTEMS	26
2.1 Biomacromolecular mass spectrometry	28
2.2 Macromolecular ion physics	30
2.3 Mass spectrometry of Art	32
3. STRUCTURE, FUNCTION AND FLOW OF SOFT MATERIALS	34
3.1 Computational physics	36
3.2 Bio-assembly and organization	38
3.3 Order/disorder in soft matter	40
3.4 Theory of complex fluids	42
3.5 Colloidal materials	44
4. NANOSTRUCTURED OPTO-ELECTRONIC MATERIALS	46
4.1 Opto-electronic materials	48
4.2 Photonic materials theory	50
4.3 Colloidal photonic materials	52
5. TRANSITION PROGRAM	54
5.1 Quantum gases	56
5.2 Molecular beams	58
6. TECHNOLOGY	60
6.1 Thin film laboratory	62
6.2 Electronics and informatics laboratory	64
6.3 Computer aided engineering department	66
6.4 Mechanical workshop	67
7. ADMINISTRATIVE AND TECHNICAL SUPPORT	68
7.1 Financial administration, personnel management, secretariat and library	70
7.2 Technical services (facility management)	71
7.3 Public relations and conference organization	72

PART 2	75
1. OUTPUT	76
1.1 Quantum dynamics of atomic and molecular systems	78
1.2 Mass spectrometry of macromolecular systems	81
1.3 Structure, function and flow of soft materials	84
1.4 Nanostructured opto-electronic materials	89
1.5 Transition program	92
1.6 Technology	94
2. PROJECTS	96
3. PERSONNEL	100

INTRODUCTION

J.T.M. Walraven
Director

The FOM Institute for Atomic and Molecular Physics (AMOLF) is one of the five national research institutes of the Foundation for Fundamental Research on Matter (FOM). The research at AMOLF is focused on selected areas of atomic, molecular and optical physics (AMO), and condensed matter physics (CM) with the aim of providing the intellectual underpinning needed to create future advanced technologies. AMOLF stimulates activities of biophysical interest.

AMOLF is an institute of approximately 100 scientists, 50 technical engineers and 25 supporting staff with an average age of 36 years. An important goal of the institute is the training of scientists and technical engineers for advanced research. This results in a steady flow of researchers and engineers to positions in industry and the academic world. Some 40 graduate students are presently active at AMOLF. They prepare for a PhD degree from one of the 6 universities in the Netherlands where AMOLF staff members hold professorships. The staff also maintains contacts with industrial partners and participates in research programs and program committees, on a national level within FOM and NWO and on an international level within the European Union. Every year, the institute welcomes many visitors from the Netherlands and abroad, and offers positions to undergraduate students and interns.

In this Annual Report an account is given of the scientific progress realized in 2000. The report is addressed, in particular, to those who support our research. By offering sufficient detail, we hope that the booklet also proves valuable to others interested in the institute, in particular our scientific visitors.

SCIENTIFIC PROGRAM

Within the central FOM organization the research has been organized in national programs. The AMOLF scientific program centers on four of these FOM programs:

- **Quantum dynamics of atomic and molecular systems (QDAMS: 1999-2002)**

This program expresses the current strength and immediate research goals of AMOLF in the domain of ultra-fast dynamics of atomic and molecular systems. Very different systems, from isolated atoms to molecules in liquid phases are investigated with light

sources ranging from the THz regime up to the XUV. Further, attention is given to the development of related instrumentation.

• **Structure, function and flow of soft materials (SFFSM: 1999-2006)**

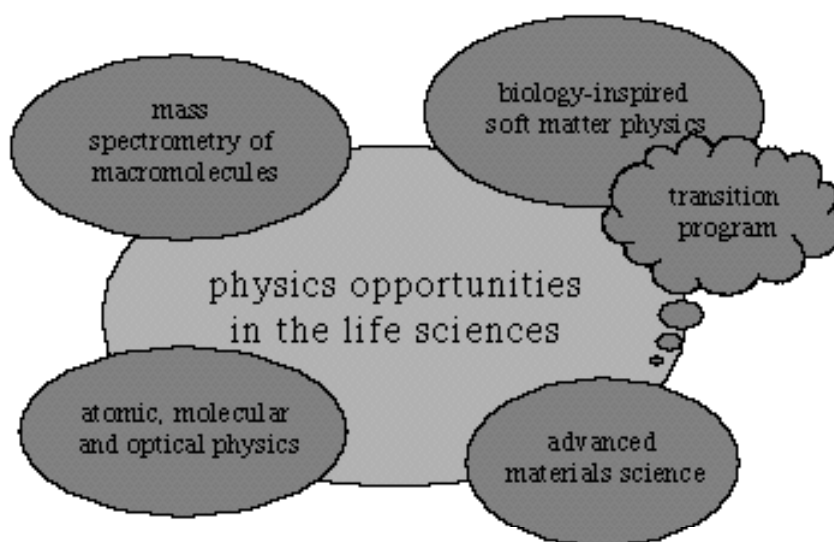
This program is aimed at gaining insight in the structural and dynamical properties of various kinds of soft materials (polymers, liquid crystals, colloidal systems and biological materials). The strength of this program is that it emphasizes the unifying aspects rather than the large differences of context and application of these materials.

• **Mass spectrometry of macromolecular systems (MS/MS: 1999-2001)**

This program is aimed at the investigation of the relationship between the function of macromolecules in polymers, polymer layers, sediments and biological materials and their chemical structure with emphasis on mass spectrometric methods. The program embodies several multidisciplinary research projects. Presently, emphasis is put on the investigation of aging phenomena in objects of painted art.

• **Nano-structured opto-electronic materials (NOEM: 1999-2003)**

This program accommodates the AMOLF interests in advanced materials with relevance for information and communication technologies. Rather than pursuing the application, the program focuses on basic research of new materials and phenomena that may become important for future application.



SPECIAL DEVELOPMENTS

The year 2000 brought several memorable events. D. Frenkel was awarded the NWO-Spinoza prize, the highest scientific award in the Netherlands, for his contributions to the development of computational physics. This recognition provides an important stimulus in particular for the computational sciences in and around AMOLF. The Chemical Science division of NWO awarded support from the prestigious NWO-Pionier program to H. Bakker. He will work out his plans in collaboration with the University of Amsterdam. M. Dogterom was appointed as professor of biomolecular physics at Leiden University.

B. Noordam surprised us all by announcing his departure from physics shortly after delivering his acceptance speech as a professor of physics at the free University. A very special event was this year's NWO Huygens lecture. For its half centennial celebration NWO selected a physics topic by inviting C. Wieman to talk on Bose-Einstein condensation. The presence of queen Beatrix added to the special character of the event. It was a personal pleasure for me as director of AMOLF and active scientist in the field of choice to present the reference lecture at this occasion.



With regard to funding, the institute was granted two major investments, one in equipment by NWO and one in personnel by FOM. Both investments enable the institute to reorient its research in the direction of the life sciences. A major "NWO-groot" investment will allow us to develop spatially resolved mass spectrometry as a new type of microscopy to image the macromolecular composition of surfaces of biological or biomedical interest. A major FOM investment will allow us to start three new groups. Here we selected directions in mass microscopy, single molecule biophysics and ultrafast conformation dynamics of biomacromolecules. These directions allow optimal cohesion with other directions of research in the institute (see figure). Further, a large FOM investment grant enabled the purchase of a scanning electron microscope.

In 2000 the institute received 12.7 million guilders in program funding from the foundation FOM. Together with an additional 4.4 million guilders in project funding from various sources this yields a total exploitation budget of 17 million guilders. The scientific output of AMOLF in 2000 is written down in some 130 publications and 4 Ph.D. theses.

SCIENTIFIC HIGHLIGHTS IN 2000

Ultrafast energy transfer in liquid water

Chemical and biochemical reactions can only occur when the reacting molecules have accumulated sufficient internal energy. Therefore the dynamics of these reactions is strongly affected by the rate of intermolecular energy transfer processes. At AMOLF we studied the dynamics of intermolecular vibrational energy transfer in liquid water using femtosecond mid-infrared pump-probe spectroscopy. It was found that the O-H stretch vibrations of the water molecules show an extremely rapid resonant intermolecular energy transfer with a characteristic transfer time below 100 femtoseconds. This transfer time is much shorter than the vibrational lifetime of the O-H stretch excitation which means that the excitation resonantly hops over many water molecules before it relaxes. (FOM program QDAMS)

To gel or not to gel in soft matter

Globular proteins resemble more-or-less spherical colloids with short-ranged attraction. There is, however, an important difference in demixing behavior between colloids and globular proteins: demixing into two (meta-stable) fluid phases has been observed in solutions of globular proteins. For colloidal suspensions, the demixing appears to be preempted by formation of a gel that arrests the phase separation. To investigate this difference we have calculated phase diagrams of a model system containing both short- and long-ranged attractions. Comparing systems with constant "effective" attractions but different ratios of the short and long-ranged contributions, we found that the presence of long-ranged attractions reduces the tendency to form a gel. The difference in demixing behavior between colloids and proteins may be related to the practice of "refractive-index matching" employed in preparing colloidal suspensions, where the long-ranged dispersion forces are effectively switched off. In contrast, no attempts have been made to switch off the long-ranged attractions between proteins. (FOM program SFFSM)

FTIR imaging spectroscopy dissects Rembrandt

Minute samples taken from paintings are often used to understand the laminated structure of a painting and its chemistry. In the multidisciplinary research project on Molecular Aspects of Aging in Objects of Painted Art (MOLART) paint cross-sections of Rembrandt paintings were successfully studied at AMOLF by Fourier transform infrared imaging (FTIR) to reveal the composition of the individual layers. Sample sizes of typically 400x400 micrometer area used. The method has been applied with diffraction limited spatial resolution to reveal the distribution of the different functional group in each layer. (FOM program MS/MS)

New perspectives for Bose-Einstein condensation in Cs

Thus far it has been impossible to observe Bose-Einstein condensation (BEC) in the Cs quantum gas. This is due to the large (negative) scattering length of the Cs-Cs interatomic interaction, which leads to a fast three-body decay of the sample. At AMOLF, Cs was studied theoretically for strongly confined conditions in a pancake-like external potential. In such quasi2D systems it turns out to be possible to modify the interatomic interaction by varying the confinement strength. It was shown to be possible to suppress the excessive 3-body losses observed in (3D) experiments and even change the sign of the mean field (this is equivalent to changing the scattering length in 3D). (Transition Program)

Coherent excitation with a train of electron pulses

An electron passing an atom generates a longitudinal electric field corresponding to a single cycle of electro-magnetic radiation. The field of the passing electron can induce transitions in the atom to all states for which the energy difference to the initial state is within the very broad power spectrum. As a result of this spectral width, excitation by electrons lacks selectivity in the population of the excited states. At AMOLF we investigated the effect of using a train of electron pulses and found that proper timing of the pulses can enhance the transfer to the excited state. This was demonstrated for a

transition from a 46s to a 45p state in rubidium driven by a train of 9 equally spaced electron pulses. (FOM program QDAMS)

Antihydrogen

At AMOLF we have developed a remarkably efficient method to recombine electrons with ions using a pulsed electric field. The idea is to make the electric field slow down the approaching charges, so that they collide slowly enough to stick together. The field is then quickly switched off to prevent it from pulling the particles apart again. This idea was tested on alkali atoms but should work equally well for the recombination of a positron with an antiproton to form antihydrogen. The performance of this pulsed-field recombination is such that for the number of positrons and anti-protons available in the traps of the ATRAP collaboration at CERN, the formation of a thousand anti-atoms would occur. This is more than enough for spectroscopic and gravity experiments on these exotic atoms. (FOM program QDAMS)

Extracting more information from satellite data

Doing science in outer space is extremely expensive. It therefore makes sense, once a scientific instrument is placed in orbit, to scrutinize every bit of data it sends back to earth. An instrument like GOME, designed to monitor the ozone layer by measuring the spectrum of sunlight reflected back from Earth through the atmosphere, does not provide enough resolution to directly recognize the individual narrow absorption lines of other atmospheric gases. At AMOLF we developed a new retrieval method for analyzing such spectra and recover the quantities of minor atmospheric gases. The method is sensitive to the temperature and pressure dependence of absorption lines and has been applied successfully to monitor precipitable water columns in the earth atmosphere. (FOM program QDAMS)

Strong exciton-erbium coupling in Er-doped Si nanocrystal/SiO₂ layers

Si nanocrystals can act as effective optical excitation sensitizers for Er in SiO₂ layers, enhancing the pump excitation cross section by more than 4 orders of magnitude. At AMOLF we performed time-dependent measurements of the nanocrystal and erbium excitation and decay rates and conclude that the exciton-erbium coupling is very strong, i.e. a nanocrystal nearby an Er ion appears "black". The exciton to Er excitation transfer rate is faster than 10^6 s^{-1} , and no more than one erbium ion can be excited per nanocrystal at the same time. (FOM program NOEM)

Transition radiation from multilayer structures

It is commonly known that when a charged particle, such as an electron, changes its velocity, it emits electromagnetic radiation. Less well known is that the same effect can be obtained by keeping the velocity of the particle constant, but changing the velocity of light in the medium around it. At AMOLF a general theory was developed to calculate radiation emitted when charged particles pass through multilayer structures. This theory derives the radiation from the first principles of electromagnetic and quantum theory,

rather than just summing the contribution of the radiation from individual interfaces. It thus takes account of many effects that are occurring in between interfaces, in the layer materials itself, such as the emission of Cerenkov radiation of X-rays. (FOM-Program NOEM)

Vibration dynamics in thin liquid-crystal films

In smectic crystals molecules are regularly stacked in layers of molecules with a fixed orientation. The structure within the layers is completely disordered, and molecules can freely flow within their own layer. Such a structure is much less rigid than that of ordinary solids, and this leads to unusual fluctuations of the layer spacing. By studying very fast fluctuations in the reflection of X-rays from a very thin smectic liquid-crystalline films it was found that, unlike in thicker films, inertia plays an important role in the vibration dynamics. The measurements were done at the ESRF in Grenoble. (FOM-Program SFFSM)

Shape matters in Bose-Einstein condensation

Tonks studied in 1936 a one-dimensional (1D) classical gas of hard spheres and showed that the hard repulsion has important consequences for the behavior of the gas. Also the 1D Bose gas turns out to have unique properties. In contrast to the situation in two- and three-dimensions, in strongly elongated harmonic traps the behavior of Bose gases with repulsive interactions becomes *less* ideal for decreasing density. This is caused by chain formation like in Tonks gas and results in a density distribution normally expected for a trapped Fermi gas (fermionization). In a theoretical study at AMOLF the properties of quasi-1D Bose gases were explored as a function of temperature and density. Aside from fermionization at the lowest densities it was found that in elongated traps Bose gases show BEC for sufficiently high density and sufficiently low temperatures, also in the presence of interactions. It turns out that in many cases where a condensate would be expected in fact a quasi-condensate forms. This is a state where the density distribution strongly resembles that of an ordinary condensate, but the quantummechanical phase fluctuates in space and time. (Transition Program)

Slow photoelectron imaging

A powerful modern technique for studying ionization or dissociation processes is velocity imaging. Charged particles originating from such processes are guided by electric fields to a detection screen. The fields are designed such that the point on the screen where they impact (recorded by a camera) depends only on their initial velocity, (not their position), and thus is a direct measurement for this quantity. In producing extremely slow electrons by ionization of metastable xenon atoms an unexpected effect was observed: the charge of the single ion from which the electron came was observed to affect the trajectory of electrons that initially moved away from the detector screen, and thus had to pass the ion once more. (FOM program QDAMS)

PART I

I. QUANTUM DYNAMICS OF ATOMIC AND MOLECULAR SYSTEMS

Program coordinator: W.J. van der Zande

The central theme of the program on the quantum dynamics of atomic and molecular systems is the investigation and manipulation of dynamical phenomena in atomic and molecular systems under conditions where quantum-mechanical behavior is important. Emphasis is put on the following aspects:

- The investigation of the dynamics in atoms and molecules at all time scales up to femtoseconds
- Optical manipulation of the internal structure of atomic and molecular systems
- Maintaining state of the art instrumentation
- Development of novel apparatus as spin-off of fundamental research

The quantum character of electronic and nuclear motion manifests itself in physics and chemistry and is therefore of fundamental importance for fields of application such as the manipulation of chemical reactions with light or the modeling of the earth atmosphere. At AMOLF, the research on quantum dynamical phenomena is motivated both from the point of fundamental interest and in view of these applications. Research momentum is optimized by sharing scientific skills and insights and by pooling of experimental apparatus.

1.1 VIBRATIONAL DYNAMICS

H.J. Bakker

This group studies the microscopic structure and dynamics of hydrogen-bonded systems in the condensed phase, like for instance liquid water. In this study, linear and nonlinear optical techniques using ultrashort pulses in the mid- and far-infrared are employed.

Hydrogen bonding is an extremely important and special type of intermolecular interaction that plays an important role in many (bio)chemical processes. In addition, the hydrogen-bond interaction determines the macroscopic physical properties of many systems in the condensed phase, like for instance liquid water. Unfortunately, most condensed-phase hydrogen-bonded systems are strongly inhomogeneous so that the microscopic structure and dynamics of these systems cannot be studied with conventional (linear) spectroscopic techniques like infrared absorption or Raman spectroscopy.

Information on the microscopic dynamics of hydrogen-bonded systems like liquid water can only be obtained using *nonlinear* optical techniques that enable the separation of the response of a selected subensemble of the molecules from the rest of the inhomogeneous ensemble. Examples of these techniques are saturation pump-probe spectroscopy, spectral-hole burning and photon-echo spectroscopy. The application of these techniques requires intense, ultrashort laser pulses of which the central frequency can be tuned to the resonance frequency of the molecular vibrations (mid-infrared, 2.5-10 μm) or the hydrogen bonds (far-infrared, 50-300 μm). An important part of the research of the group is concerned with the development of new light sources that are active in this frequency region.

In the past, we have studied the microscopic structure and dynamics of pure liquid water (H_2O) and isotopically diluted water (HDO dissolved in D_2O and HDO dissolved in H_2O) using intense femtosecond laser pulses with a central wavelength of 3 μm (resonant with the O-H stretch vibration) and 4 μm (resonant with the O-D stretch vibration). For these systems, we studied the time scale on which the hydrogen bonds stretch and contract, i.e. the time on which the water molecules move with respect to each other. For liquid water, we found a characteristic time scale of 400 femtoseconds, for deuterated water of 500 femtoseconds. We also observed that these hydrogen-bond stretching dynamics are strongly coupled to the reorientational motion of the water molecules. This coupling turns out to be responsible for the non-Arrhenius character of the temperature dependence of the reorientation rate. In addition, we studied the thermalization dynamics of water and other hydrogen-bonded liquids following a local deposition of energy. This thermalization involves a change of the relative positions and orientations of the molecules. For water, the equilibration has a characteristic time scale of 0.55 picoseconds, and is much faster than for other hydrogen-bonded liquids like alcohols. Polarization-sensitive pump-probe experiments showed that the O-H stretch vibrations of the water molecules show an extremely rapid resonant intermolecular energy transfer with a characteristic transfer time below 100 femtoseconds. This transfer time is much shorter than the vibrational lifetime of the O-H stretch excitation, which means that the vibrational excitation hops over many water molecules before it is transferred to other degrees of freedom, e.g. the hydrogen bonds.

More recently, we have studied the dynamics of water molecules in solvation shells of halogenic ions (Cl^- , Br^- , I^-), hydroxide ions (OH^-) and protons. Aqueous solvation interactions are believed to play a crucial role in

chemical reactions and in the determination of the three-dimensional structure of large complicated structures like proteins. A severe complication in studying aqueous solvation dynamics is that it is very difficult to distinguish the response of the solvating water molecules from the bulk water. However, we discovered that two-color femtosecond saturation spectroscopy can form a very effective tool in selectively measuring the response of solvating water molecules. We found that the vibrational lifetime of the O-H stretch vibration of water molecules in the first solvation shell of the halogenic anions Cl^- , Br^- and I^- is 2.3, 2.7 and 3.0 picoseconds, respectively. These lifetimes are much longer than the vibrational lifetime of bulk water molecules, for which we measure 740 femtoseconds. As a result, after a few picoseconds only the response of the solvating water molecules is observed, which enables a detailed, selective study of the structure and the dynamics of these molecules. We found that the solvation shell of the anions is surprisingly rigid and well-defined: the rate at which the distance between the anion and the solvating water molecules is modulated is approximately 30 times smaller than the rate at which the hydrogen-bond length between two water molecules in bulk water changes.

INVESTIGATORS : F. van den Broek, H.K. Nienhuys, A. Lock and M. Kropman

TECHNICAL SUPPORT : H. Schoenmaker and R. Kemper

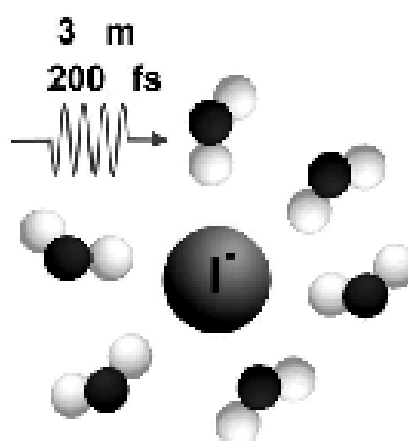


Fig. 1: Schematic picture of a pulsed mid-infrared excitation of a water molecule in the first solvation shell of the I^- anion.

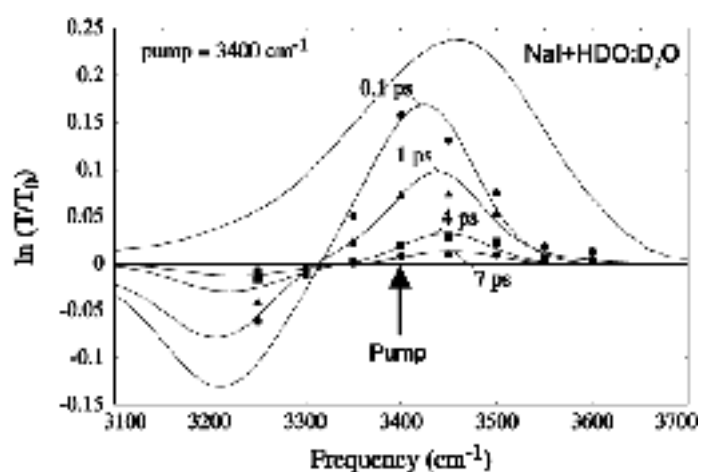


Fig. 2: Spectral hole burning experiment on the O-H stretch vibration of a solution of NaI and HDO dissolved in D_2O . The spectral hole induced by the femtosecond mid-IR pump pulse with a central frequency of 3400 cm^{-1} ($=2.94\text{ }\mu\text{m}$) is much narrower than the linear absorption spectrum (dashed curve), indicating the strongly inhomogeneous character of the absorption band. With increasing time delay, the hole shifts and broadens, which reflects hydrogen-bond dynamics.

1.2 EXTREME ULTRAVIOLET PHYSICS

M.J.J. Vrakking

This group investigates the fundamental mechanisms of extreme ultraviolet (XUV) and X-ray generation based on the interaction of ultra-intense femtosecond laser pulses with gaseous media (high harmonic generation) and condensed phase media (laser plasma formation in clusters and liquids). This research offers unique new inroads for studies of molecular reaction dynamics, time-resolved molecular photoionization and photodissociation, and time-resolved X-ray diffraction.

In recent years intense femtosecond lasers have provided many new opportunities in studies of molecular dynamics. On one hand, there are rapid advances in the way intense femtosecond lasers are used to generate ultrashort pulses in the soft and hard x-ray regime. These pulses show considerable promise for applications in particular in chemical research. At the same time, there are many new and exciting developments in studies of the direct interaction of intense femtosecond lasers with individual molecules. Recent years have seen experiments where Coulomb explosions were used to follow the progress of a molecular dissociation in real time, and intense femtosecond lasers are increasingly finding applications in mass spectrometry, due to the lack of parent fragmentation in multi-photon ionization with femtosecond versus nanosecond lasers. One aspect of the interaction of intense femtosecond lasers with molecules which is attracting considerable interest, is the aspect of control. At the focus of an intense laser, oscillating electric fields are present that are comparable to or may even exceed the electrostatic fields experienced by the electrons in an atom or molecule. As a result, molecules are strongly polarized in an intense laser field, and experience driving forces that have the tendency to both trap and align them. Several groups in the world are considering the application of intense laser fields in what has sometimes been called 'molecular optics'.

Recently we have started a series of experiments to study alignment of molecules in intense laser fields using ion imaging. In the first experiment we have studied kinetic energy and angular distributions in multi-electron dissociative ionization of I_2 and Br_2 as a function of the duration and energy of the intense near-IR femtosecond/picosecond laser pulse used. Singly and doubly charged atomic fragments were recorded using the velocity map ion imaging detector which we previously applied to the detection of slow photoelectrons resulting from the photoionization of metastable Xe atoms (PRL 85, 4023 (2000)). As figure 1 illustrates a significant narrowing in the angular distributions was observed when the pulse durations were increased from 100 femtoseconds to about 1 picosecond. In these experiments, the angular distribution is due to a combination of three effects, namely (i) a possible laser-induced ground state alignment, (ii) the angular dependence of the molecular ionization and (iii) the angular dependence of the subsequent Coulomb explosion. While the analysis is currently still in progress, we believe that the significant narrowing of the angular distribution for longer pulses is a manifestation of the fact that under these conditions the molecules have a longer time to adapt to the potential well generated by the laser, i.e. the narrower angular distributions are a manifestation of alignment of the molecules in their ground electronic state prior to the loss of the first electron. After ionization the singly-charged molecular ions dissociate until they reach a critical distance (which typically is about 5 Å) where the laser intensity needed for further ionization (i.e. Coulomb explosion) is minimal. Due to the existence of this critical distance, a widening of the angular distribution is predicted in the absence of ground state alignment, quite contrary to what is observed experimentally. Hence the conclusion is drawn that ground state alignment prior to ionization is an important factor in these experiments.

Building on the understanding gained in the experiments discussed above, we have also recently carried out a two-laser pump-probe experiment in which the alignment induced by a relatively long near-IR pump pulse (1-10 ps) was probed using multi-electron dissociative ionization with a short probe pulse (80 fs). These experiments showed the onset of alignment during the pump pulse (see Fig. 2), and importantly, revealed the formation of a rotational wavepacket by the pump pulse, leading to periodic recurrences of the alignment at characteristic time delays following the pump pulse. The observation of these recurrences is particularly significant, since it allows us to prepare aligned molecules under field-free conditions, paving the way to studies of angular-resolved molecular photoionization and photo-dissociation in the molecular frame.

INVESTIGATORS : C.C.S. Nicole, H.L. Offerhaus, E. Springate, F. Rosca-Pruna, A.J. Houtepen, M. Krishnamurthy, N. Farid and M. Pereira

TECHNICAL SUPPORT : R. Kemper and A.N. Buijserd

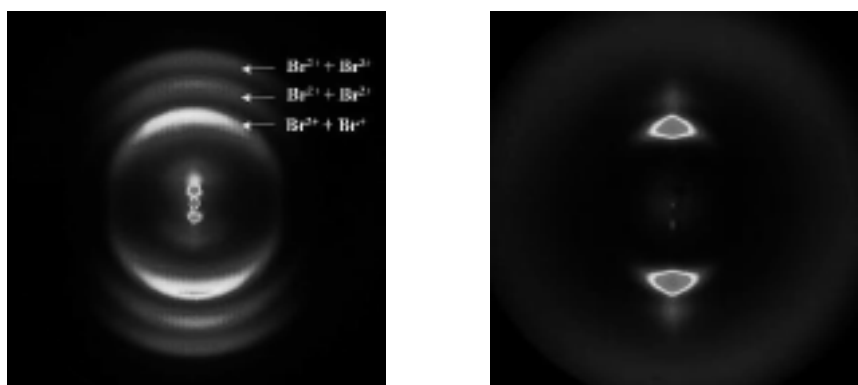


Fig. 1: 2D ion images for multi-electron dissociative ionization of Br_2 using 100 femtosecond (left) and 1 picosecond (right) pulses, respectively. The 2D images show the projection of the 3D velocity distribution of the Br^{2+} fragments. The rings in the images correspond to Br^{2+} ions which are formed together with Br^+ , Br^{2+} and Br^{3+} , respectively. The angular distribution with respect to the vertical axis (which coincides with the laser polarization axis) narrows as the Br_2 molecules are aligned prior to ionization.

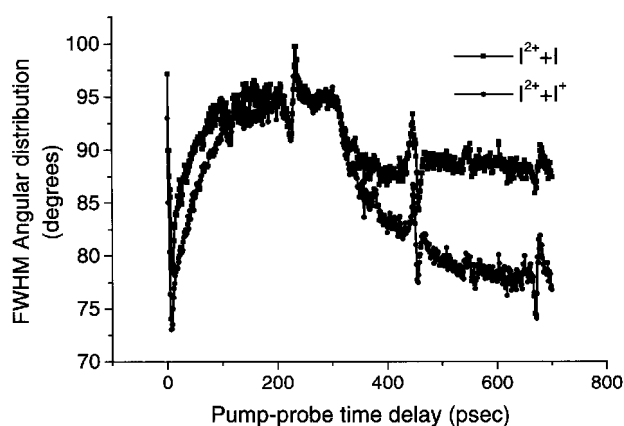


Fig. 2: Width of the angular distribution of two charge-channels in the multi-electron dissociative ionization of I_2 as a function of the delay between a 7 ps pump laser, which alters the alignment of the ground state I_2 molecules without ionizing the molecules, and a 80 fs probe laser, which ionizes the molecules with little modification of the alignment. It is observed how at zero time-delay the molecules are aligned by the pump laser, and how at long time delays (225, 450 and 675 ps) revivals occur of the rotational wavepacket that is formed by the pump laser.

1.3 ATOMS IN STRONG RADIATION

H.G. Muller

This group studies the behavior of atoms, molecules or clusters under irradiation by super-intense light. Of special interest are those situations where the force exerted by the electromagnetic radiation exceeds the forces that keep an atom together. Modern laser technology makes it possible to achieve such situations even for the most resistant atoms.

Computer simulations are growing into an ever more useful approach to understanding the behavior of atoms in super-intense situations. Calculations provide a level of detail that can not be obtained yet from experimental studies, such as making a movie of the behavior of a wave function on a sub-femtosecond time scale with sub-Ångstrom resolution. We have developed new, efficient numerical algorithms for solving the time-dependent Schrödinger equation of electrons in the presence of fields. This makes it possible to generate essentially exact solutions for the behavior of a single electron in a truly three-dimensional potential, in a volume large enough to contain the asymptotic region (where interaction between electron and parent ion become negligible). Research now focuses on (even more complicated) two-electron systems: double ionization of helium by linearly polarized light can be reduced to a five-dimensional problem, and a computer code to solve this problem is now partly completed and has produced its first (approximate) results.

Super-intense conditions can under some circumstances enhance the stability of an atom against ionization. This effect, known as stabilization, was initially predicted on the basis of approximate theoretical methods. It is now being studied more quantitatively by precision simulations. This is done in cooperation with M. Gavrila (Harvard) and M. Dondera (Bucharest). Experiments on this subject are in a preparation stage: this year a new electron spectrometer was built, for the purpose of doing angle-resolved field-free or retarding-field time-of-flight spectroscopy, as well as ion time-of-flight measurements.

Another experiment studies the Coulomb explosion of Van der Waals clusters of molecules. Such explosions occur when a laser "boils off" a large number of electrons from a cluster, the remaining positive charge creating a very deep potential well that then traps the rest of the electrons. The thus created plasma can be heated by a laser very strongly before it disperses into highly-charged ions, and this could provide an ideal first step for an X-ray laser. We have focused mainly on clusters of propane (C_3H_8) and CO_2 , and studied the charge state and kinetic energy of the remaining carbon ions. Up to C^{5+} was observed from our cluster expansion, and we are currently interpreting cluster-size measurements based on Rayleigh scattering to better explain the data.

In a cooperation with P. Agostini (Saclay), we studied the time dependence of high-harmonic radiation which is generated by atoms irradiated with an intense short-pulse laser. The generated harmonic pulses were already known to be much shorter than those of the driving laser, and thus are among the shortest pulses ever generated. They fall in the extreme ultraviolet (XUV) range of the spectrum, which is very hard to handle. We developed a novel way to perform pulse-duration measurements on such pulses, based on the rapid change of the ionization potential of an atom in an optical light pulse ("ponderomotive streaking"). The energy with which photo-electrons liberated by the XUV appear then identifies the time of emission. In another experiment (also performed at Laboratoire d'Optique Appliquée in Palaiseau), we succeeded in

measuring the relative phases of several harmonics, by measuring the interference between multiphoton processes involving different harmonics as well as photons from the driving laser. Knowing these phases enables one to calculate the exact time dependence of the XUV field (the intensities of the various harmonics are trivially obtained from the spectrum).

INVESTIGATORS : E.S. Toma, L.C. Dinu and M. Kalinski

COOPERATION PARTNERS : M. Gavrila, M. Dondera and P. Agostini

H.G. Muller is also professor of physics at the Free University of Amsterdam.

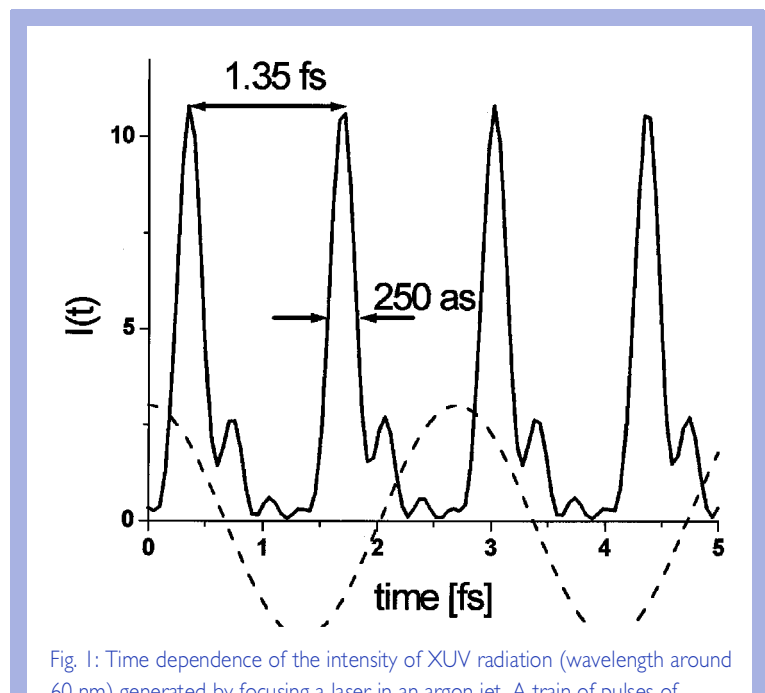


Fig. 1: Time dependence of the intensity of XUV radiation (wavelength around 60 nm) generated by focusing a laser in an argon jet. A train of pulses of 240 attoseconds in duration results.

1.4 FEMTO-PHYSICS

L.D. Noordam

Atoms with sufficient internal energy can break apart into an ion and an electron. It is the aim of our research to study and control this ultra-fast decay process. In the experiments atoms and small molecules are excited with ultra-short, pulsed laser or electron beams. We investigate whether and when the excited neutral breaks apart into an ion and an electron. We also study the inverse process, recombining an electron and an ion to make a neutral atom.

Making an (anti-) hydrogen atom by combining an electron and a positive ion is not simple. The recombination is only possible when a third object carries away the excess energy of the captured electron. This third particle can be a second, spectating, electron (three-body recombination), or a photon (radiative recombination). We have developed a new recombination method: suppose an electron is approaching a proton in the presence of an electric field, such that the electron just passes over the saddle point of the barrier. A quasi-bound state is formed and eventually the electron will leave the potential over the same barrier. The lifetime of these quasi-bound states is relatively long: $n = 200$, $\tau = 1.2$ ns. To achieve recombination one has to reduce the static field while the electron is quasi bound. The electron is captured below the (reduced) saddle point in a Rydberg state. We have demonstrated (see Fig. 1) a recombination efficiency of 2%, which is orders of magnitudes bigger than achieved by other methods in the past. The ATRAP collaboration at CERN operates a magnetic trap in which antiprotons and positrons are stored in two adjacent volumes. In order to make neutral anti hydrogen, we have implemented the pulsed field recombination experiment in the trap at CERN. Attempts to make cold antihydrogen atoms at CERN by means of PFR are ongoing.

Using a short optical pulse one can excite a Rydberg wavepacket, thus exciting the electron from a low-lying state to a coherent superposition of high-lying states. In the case of a weak half-cycle THz pulse interacting with a stationary Rydberg state, a special kind of Rydberg wavepacket, the THz wavepacket is generated. This THz wavepacket is a coherent superposition of the initial Rydberg state and its neighboring states. We have investigated the time evolution of THz wavepackets by measuring the impact of a second, delayed, half-cycle pulse on the population of the Rydberg states. The first half-cycle pulse creates the THz wavepacket and the second half-cycle pulse probes the dynamics of the THz wavepacket. We found (see Fig. 2) that the THz wavepacket is initially delocalized and becomes localized after half a revival time, whereas a conventional optical wavepacket starts localized and becomes delocalized.

Driving transitions among Rydberg states can also be achieved by electron collisions. We are currently investigating how to get control over such transitions. The Coulomb field of an electron passing an atom generates a transverse electric field of a half cycle and a longitudinal field corresponding to a single cycle pulse. These fields induce transitions within the atom. The power spectrum of the radiation of a single-cycle pulse is very broad: the field of the passing electron can induce transitions in the atom to all states for which the energy difference to the initial state, E , is within the generated power spectrum. As a result, collisional excitation lacks selectivity in the population of the excited states. In our search for a scheme to control the excited state population we are inspired by the success of controlled photoexcitation using narrow-band lasers. We investigate if enhanced excitation of a selected state is also possible for electron collisions and thus turn the (inefficient) broadband excitation into controlled excitation. To this end we consider the impact of a

train of electron pulses with a repetition frequency ν . As in the optical case, this will induce a series of N broadband bursts of radiation spectrum. We have shown that the analogy with photons holds and N bursts spaced with time $\tau = 1/\nu$ will also favor transitions with frequency $\omega = 1/\tau$.

As applications of this breaking of atoms we built an XUV spectrometer based on an atomic detector, see Fig. 3. The XUV photon excites high Rydberg states of neon in the spectrometer. The atoms are placed in an electric field. This field lowers the ionization threshold. By measuring the electron yield at different field strengths and taking the derivative of the yield versus binding energy, one obtains the spectral profile of the XUV pulse. This simple method has a remarkable resolution of $\Delta E/E = 10^{-5}$.

INVESTIGATORS : C. Conover, A. Guertler, M. Warntjes, K. Wesdorp and A. Wetzels

TECHNICAL SUPPORT : A.N. Buijserd, R. Kemper and H. Schoenmaker

L. D. Noordam also professor of physics and chemistry at the Free University of Amsterdam, and consultant for McKinsey&Company.

Fig. 1: Demonstration of Pulsed Field Recombination of Li atoms and electrons. The exact closing time of the Coulomb-Field potential to frustrate the escape of the Rydberg electron is quite essential.

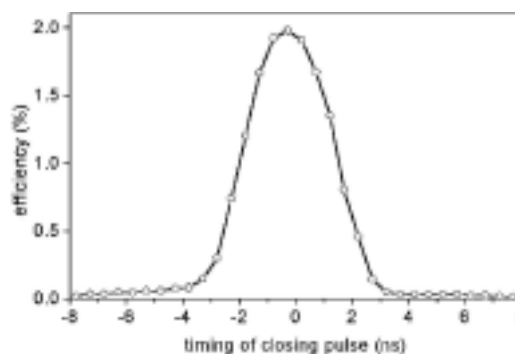


Fig. 2: A demonstration of the special feature of THz wavepackets. Initially (delay = 0) the wavepacket is dispersed and no oscillation in the population of the states is observed, whereas after about 60 ps the wavepacket has collapsed and shows a clear oscillation. The oscillation time matches the Kepler orbit time of the Rydberg electron.

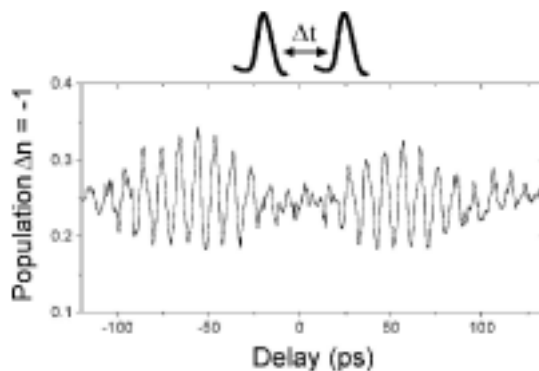
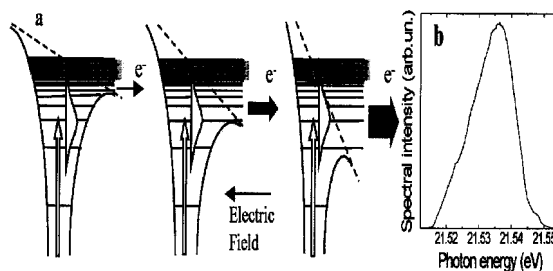


Fig. 3: Neon atoms are used to determine the spectrum of the XUV photon (see also text).



1.5 ATMOSPHERIC PHOTOPHYSICS

W.J. van der Zande

We focus on quantitative molecular and atmospheric physics. Experimental studies are performed on the behavior of small molecules under the influence of visible and UV radiation and of small molecular ions upon collisions with thermal electrons. Numerical studies are performed on radiation transport and the determination of trace gas concentrations in the atmosphere from satellite data.

The response of molecules on light and on electrons are essential in many aspects of the composition and dynamics of the earth's atmosphere. Possible heating of the atmosphere, the formation of the ozone hole, the strength of aurorae; all these phenomena can be related to elementary molecular processes. Many molecules are excited by solar light. This fact is employed for diagnostic purposes. These elementary processes offer fascinating opportunities for fundamental research and generate a continuous demand for experimental innovations.

Collisions of gaseous thermal electrons and molecular ions take place in our ionosphere continuously. This process is called dissociative recombination (DR). DR is responsible for much of the airglow in the upper atmosphere through the formation of excited atoms that emit light. The experiments are performed on the heavy ion storage ring CRYRING in the Manne Siegbahn Laboratory (Stockholm University) in collaboration with M. Larsson. In 2000, we have determined the product states for nitric oxide ions (NO^+), the most abundant of all atmospheric molecular ions, and for oxygen ions (O_2^+). It turns out that highly reactive atomic fragments are generated in these processes. We found that resonances in this process influence diagnostics of the ionosphere using the airglow of oxygen atoms. The DR process involving triatomic species has presented very surprising results; these tri-atomic species prefer to break up in three fragments. We have characterized the product oxygen atom in DR involving water ions; an important result on the way to understanding the important three-fragment channel. The latter experiment required an analysis of the dynamics of a three-body break-up.

In AMOLF, experiments were performed using fast beam-photofragmentation. We have chosen in 2000 to study DR in molecular hydrogen via photo-excitation of triplet molecular hydrogen. Using UV photo-excitation, triplet molecular hydrogen is excited just above the ionization energy. We observed competition between auto-ionization ($\longrightarrow \text{H}_2^+ + e^-$) and dissociation ($\longrightarrow \text{H}(n=2) + \text{H}$). This observation implies that the inverse process of auto-ionization is also coupled to molecular dissociation. The combination of the inverse process of auto-ionization and dissociation is simply dissociative recombination. In collaboration with D. Parker (University of Nijmegen) we have finalized our studies into dissociative ionization of molecular hydrogen using velocity map ion imaging.

In 1998 we started a research program to provide a more direct link between laboratory data and satellite observations. The Netherlands is responsible for two very advanced satellite spectrometers, GOME (in operation since 1995) and SCIAMACHY (to be launched in 2001). In 1999 and in 2000 new numerical techniques have been developed and tested for the analysis of water concentrations using a weak absorption band in the visible from GOME. This provided the first possibility to add water to the detectable trace gasses using this global experiment. This work is a close collaboration with the group of W. Ubachs at the Free

University in Amsterdam and with I. Aben at the Space Research Organization Netherlands (SRON), and involves analysis of satellite data, cavity ring down spectroscopy, XUV spectroscopy and photo-fragment spectroscopy.

In 2001, we will focus our research in DR on molecular oxygen. Photo-fragment studies will be performed on neutral atmospheric molecules such as oxygen and ozone. Our numerical activities on satellite data will be extended to the analysis of emission phenomena, whereas extra experimental efforts will go towards quantitative cavity ringdown spectroscopy and a new experiment studying light scattering of non-spherical particles. Our instrumental efforts will be directed towards novel schemes of multi-particle detection and the development of a fast and efficient infrared camera.

INVESTIGATORS : R. Lang, L. Dinu, A. Petrigani, R. Thomas, A.N. Maurellis and Y. Picard

TECHNICAL SUPPORT : I. Stavenuiter, A. de Snaijer and A. Meijer

W.J. van der Zande is also professor of physics at the Catholic University of Nijmegen.

Fig. 1: The strength of the oxygen green airglow in the night sky depends on the electron density, the number of oxygen ions, the collision cross section and the relative efficiency of the formation of excited oxygen atoms. This figure reveals that the latter is an unexpected function of the electron temperature with a minimum around 200 K.

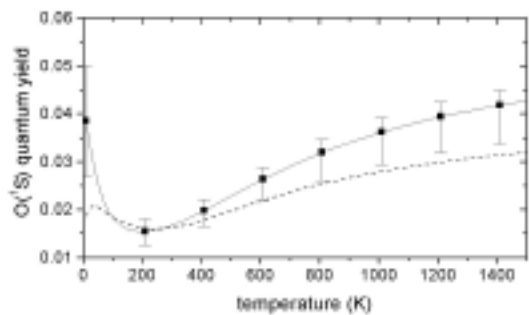


Fig. 2: If sufficient energy is attributed to a molecule, it can dissociate or ionize. The competition between these processes reveals among others what happens in collisions of molecular ions with free electrons. Using UV light we excite molecular hydrogen to high-lying molecular Rydberg states in a fast beam. With the aid of camera techniques we can distinguish between the formation of an ion with an electron and two neutral fragments. This figure shows a small wavelength scan containing both processes and reveals that the amount of dissociation is not constant for all excited states.

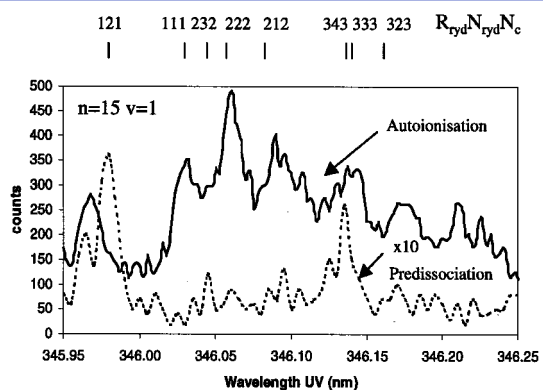
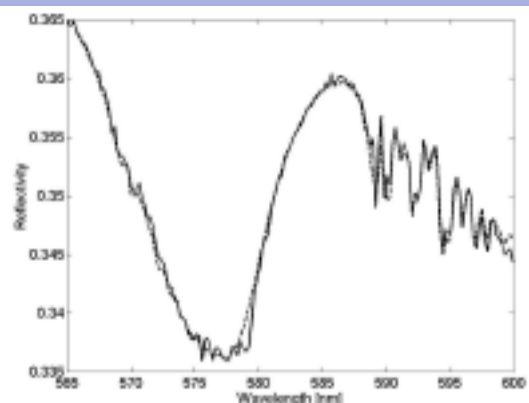


Fig. 3: Part of a GOME spectrum in the visible region of the spectrum, detecting sunlight reflected from the earth surface. This part of the spectrum is affected by the presence of ozone, O₃, the collision complex of oxygen, (O₂)₂, atomic sodium, gaseous water, Rayleigh scattering and the color of the earth (albedo). The dashed line reveals how well this spectrum can be reproduced. This makes it possible to use this information to obtain total water amounts in our atmosphere.



**2. MASS SPECTROMETRY
OF
MACROMOLECULAR SYSTEMS**

Program coordinator: J.J. Boon

The research objectives of this program are the study of ion physical aspects of the mass spectrometry of large polymers and biomolecules, the development of new mass spectrometric methodologies for multidisciplinary biological and environmental studies, and the study of paintings and other art objects using advanced mass spectrometric and imaging spectroscopic methods. A special focus of the ion physical studies is the accurate manipulation and determination of internal energies in model systems and macromolecular ions in various collision-induced dissociation processes. The macromolecule studies concern matrix assisted laser desorption ionization and electrospray studies of lipids, proteins and synthetic polymers using high resolution Fourier transform mass spectrometry for extraction of information on the sequence of monomeric units, the three dimensional structure and non-covalent interactions of the polymers. Our collaborative environmental studies are focussed on the mass spectrometric characterization of estuarine and oceanic dissolved organic colloidal matter. A central theme in the multidisciplinary MOLART project on aging processes in paintings is a fundamental study on the present molecular condition of the materials in paintings, which have changed in the course of time as a result of oxidation and cross-linking processes.

2.1 FUNDAMENTAL ASPECTS OF MASS SPECTROMETRY AND ION PHYSICS OF MACROMOLECULES

R.M.A. Heeren

The aim of this research is to determine the activation and dissociation energies of high molecular weight bio-macromolecular complexes to gain insight into the structure and function of a wide scope of polymeric systems ranging from peptides and proteins to industrial synthetic polymers. The various research topics include the investigation of fundamental processes of ion formation, ion dissociation, mass separation and detection of macromolecules to improve the derivation of structural information and to understand the binding energy relationships involved in the association of macromolecules. FTICR-MS as a stand-alone high resolution laboratory for macromolecular ion physics offers the unique combination of high speed, high resolution and high accuracy mass analysis, in addition to non-destructive, multi-channel ion detection and the structural analysis of selected ions by MSⁿ. Gas-phase activation studies on trapped and purified macromolecular complexes can link the bond energies with structural information. Ion-molecule reactions of gas-phase complexes probe the non-covalent interactions of macromolecular protein-protein, protein-substrate and protein-DNA complexes, thus linking the gas-phase behavior to the solution phase behavior.

INTERNAL ENERGY STUDIES OF MACROMOLECULES

In 2000 the internal energy studies on macromolecules focused on the determination of thermal activation energies using a newly developed thermostated ICR cell. Different pump-probe schemes were explored to accurately manipulate the internal energy of small peptides such as leucine-enkephaline. A comparative study between the new cell and the original (commercial) ICR cell showed that the Boltzmann temperature could be manipulated with an accuracy better than 1 degree. A novel variation on the activated ion dissociation technique was developed in which the ions were thermally excited by continuously increasing the ambient temperature and subsequently fragmented with fixed collision energy (see Fig. 1). This allows us to determine the internal energy dependence of the dissociation rate. The determination of the relaxation rate with activated ion dissociation continued to demonstrate that a hotter ion population exhibits a much higher internal energy relaxation rate than a cold ion population. A set of experiments was performed to prove that the main internal energy loss mechanism was the emission of Infrared radiation.

In collaboration with the group of Nanninga of the UvA a series of ESI-FTMS studies was performed aimed at the determination of the phospholipid composition near cell division sites in *E. coli*. Tandem mass spectrometric studies were employed to determine the polar head groups of the individual phospholipid species. Quantification (without internal standards) of the cardiolipin species did not show any alternation of the composition between mini-cell mutant *E. coli* and the wild-type cells within the margin of error of the measurement.

To extend the internal energy studies an new SID system was developed for ion dissociation studies of macromolecular ions produced by MALDI.

MASS SPECTROMETRY OF SYNTHETIC POLYMERS

The applicability of ESI-FTICRMS as an analytical tool for various classes of synthetic polymers studied as collaborative project with AKZO-NOBEL and DSM. Fundamental studies on the dissociation behavior of electrosprayed polymers were continued during 2000. A highlight in these studies was the MSⁿ experiment performed on hyperbranched polyesteramides. These molecules are made by the polycondensation of the

trifunctional diisopropanolamine with the difunctional anhydrides of adipic acid, succinic acid, glutaric acid, 1,2-dicarboxylic acid cyclohexane and phthalic acid. The fragmentation pathways described by de Koster et al. in JASMS 2000 have all been observed. By constructing breakdown diagrams, it was observed that the lowest energetic fragmentation pathway is the loss of H₂O followed by ester and amide bond rearrangements. The loss of a second H₂O has highest onset energy. These fragmentation mechanisms were used to determine the polymerization defects in hyperbranched polyesteramides.

ARBITRARY WAVEFORM GENERATION AND TRANSIENT DIGITIZATION

New possibilities for ion isolation and manipulation in the ICR cell were made possible by development of an unique arbitrary waveform generator and control software by the AMOLF E&I group. The 192 megabyte memory module allows the generation of an arbitrary number of high resolution RF excitation pulses. During 2000 the AWG/TD was expanded with a set of 4 digital down converters (DDC). This addition to the system now enables us to perform 4 digital heterodyne experiments simultaneously on the same ion population. The software for detection and visualization was further improved in order to be able to deal with the complex and real parts of the transients measured with the DDC's. The ion isolation capabilities of the AWG/TD were employed in our group to support the internal energy studies as well as the synthetic polymer studies.

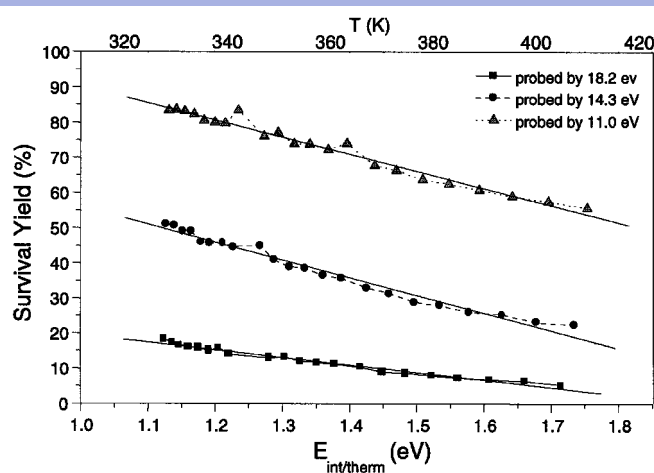
VIRTUAL LABORATORY DEVELOPMENTS IN ICES-KIS

The aim of the Virtual laboratory (VL) project is to make large scale instrumentation, database and mathematical modeling results available accessible irrespective of the location of the scientist requiring this infrastructure. This became possible through advanced internet connections (Giganet). Combining several sources of scientific information creates new possibilities for the analysis of complex and distributed data. A database model was set up around a generic data-cube which will allow us in the future to incorporate other large datasets with a high information density into the VL database. Additionally, several chemometric tools were developed to examine these generic data cubes and generate meta-data in the form of principle components extracted from three data sets. This meta-data by itself will be embedded in a separate database. The strength of the VL is that results from different scientific experiments can be readily combined to provide new insights and improve the quality of the individual datasets.

INVESTIGATORS : X. Guo, A. Al-Khalili, S. Koster, A. Kleinnijenhuis, C.M. Koppelmans (UvA), G. Eijkel and P.G. Kistemaker.

TECHNICAL SUPPORT : M.C. Duursma,
A. de Snaijer, W. Barsingerhorn
and A. Kerkhoff

Fig.1: Three infrared activated ion dissociation experiments on Leucine Enkephalin. The Boltzmann temperature of the ion population was varied between 330 K and 410 K. This resulted in a change in internal energy from 1.1 eV to 1.75 eV. The activated ion population were probed with three different collision energies, 11.0 eV (squares), 14.3 eV (circles) and 18.2 eV (triangles) respectively. Each case demonstrated a linear dependence of the internal energy with the Boltzmann temperature.



2.2 BIOLOGICAL AND ENVIRONMENTAL MASS SPECTROMETRY

J.J. Boon

The research is focussed on bacterial, algal or plant derived biomolecules exposed in the environment that have been modified into covalently cross-linked complexes. These complexes are investigated with pyrolysis mass spectrometry and related spectrometric techniques.

The technique of Direct Temperature resolved Mass Spectrometry (DTMS) allows the direct characterization of particulate and colloidal fractions. The instrumentation was upgraded this year to a four sector MSMS system and enabled us now to perform high resolution mass spectrometric studies of the ions and precursor ion fragmentation studies in MSMS mode. This opens completely new horizons. Exploratory studies were performed with MALDI techniques using TOF and ITMS on the imaging of peptide and proteins on RP-C18 surfaces.

BIOMACROMOLECULES IN SEAWATER

Dissolved organic carbon (DOM) is the largest reservoir of carbon in the ocean and is comparable to the amount of CO₂ in the atmosphere (about 7x10¹⁷ gram). Much of this DOM remains to be identified at the molecular level. The chemical composition of more than 90 % of the organic nitrogen in the ocean is unknown. Most of the organic carbon derives from algal primary production, but much of it is recycled by bacteria, that leave their own imprint on the molecular signature in the form of biofilms, biocapsules, and cell wall remains. Mass spectrometry has so far been the only method that can extract a wide range of molecular data from the tiniest amounts of sample available. We collaborate in this field with G. Herndle of the Netherlands Institute for Sea Research (Texel), L. Minor of Old Dominion University (USA), R. Harvey of Cheseapeake Peake Bay Marine station (U of Maryland, USA), T. Eglinton of the Woods Hole Oceanographic Institution (USA) and Benner (University of S.Carolina, USA). This year Harvey spent a Fullbright Fellowship at AMOLF to study the composition of colloidal fractions in experimental ecosystems (mesocosms). Seawater was enriched with protein or algal DOM and inoculated with bacteria isolated from seawater. Ultrafiltrates with MW larger than 5000 Dalton was isolated and prepared for analysis by MS. MALDI-MS demonstrated the rapid turnover of the planted protein and the appearance of new proteins. DTMSMS confirmed the turnover of the proteins but also showed the generation of condensed oligosaccharides not unlike those observed in field samples. DT-HRMS and DTMSMS casted complete new light on the rapid changes in the composition of the chemical building blocks of the DOM as a function of incubation time. The studies will be continue with DOM from mesocosm systems in which protein enrichment was avoided.

ARCHEOLOGICAL OBJECTS

Our earlier work on residues in ancient pottery was resumed. Guest scientist T. Oudemans is working on DTMS data obtained earlier in preparation of her PhD degree. Diepenveen and Abbink requested some DTMS work on residues of pots unearthed in the Broekpolder (NL). Wiepking of the Archeologisch Diensten Centrum and H. Kars (VU) of the Rijksdienst Oudheidkundig Bodemonderzoek (ROB) requested MS studies on residues present on roman pottery.

F. Braatpaardt is performing studies as a guest researcher on charred peas that are often found at archeological sites. This is a joint project with Leiden and Utrecht University. Peas from field sites are compared with peas charred under controlled conditions. The AMOLF group contributed DTMS and FTIR data that show compositional changes comparable to our earlier work on charring of cellulose.

Studies were performed with I. Joosten from ROB to identify a dark substance inside an wooden artefact of 7000 BC, presumably a part of an ax. Comparative studies on the outside and inside of the wooden part revealed that the wood of the hole in the wood had been partially charred. The lignin signature of the hard wood was completely changed as a result of some heating process used to make the hole. The earlier idea that tar was present in the hole could be rejected.

Ambers from Rijversijde in Belgium were investigated by DTMS and FTIR. Non-destructive reflection FTIR studies of an amber ring produced puzzling spectra. Further comparative work with various Baltic ambers demonstrated that the reflection FTIR was very sensitive to oxidized surface layers. The same features were found on an amber bead from a tomb in the Mycenaean period (about 1000 BC). Below the surface layer, the usual FTIR data for Baltic ambers could be obtained. The phenomenon will be investigated further with resins and varnishes aged under controlled conditions.

SUPPORT TO INDUSTRY

Our group supported Billiton Aluminium BV in their search to solve a problem in their bauxite work-up plant. Several analyses were performed on crystalline precipitates and black sludge that forms a nuisance in the production line. The sludge was identified as a cross-linked network of aromatic hydrocarbons.

INSTRUMENTAL COLLABORATION

We have agreed with the company LPS Benelux BV in the Netherlands to exchange knowledge on the construction of pyrolysis devices and the testing of power supplies.

INVESTIGATORS : R. Harvey (Fullbright Fellow), T. Oudemans, F. Braadbaart and S. Oonk

TECHNICAL SUPPORT : G. Eijkel, J. van der Horst, M.C. Duursma and A. Kerkhoff

J.J. Boon is also professor of biology at the University of Amsterdam

2.3 MASS SPECTROMETRY OF ART

J.J.Boon and R.M.A. Heeren

Paintings, an important component of our cultural heritage, undergo undesirable physical and chemical changes that effect their esthetic quality. The AMOLF MS group is undertaking fundamental studies into the molecular aspects of aging in paintings with a special focus on oxidative changes and processes of cross-linking in the organic fractions of traditional paint.

The AMOLF research on objects of art is part of MOLART, the NWO Priority program on Molecular aspects of Aging in Art. One of the task of MOLART is the determination of the present chemical and physical condition of works of art produced in the period from the 15th to the 20th century. Fundamental studies are undertaken to understand the molecular aspects of aging since this is thought to be a main cause for the continued need to treat paintings. Quantification of the changes in chemical structure across the varnish, paint layers, grounds and support is therefore an important objective within MOLART. Processes of chemical change are studied by direct mass spectrometric techniques on homogenized samples and/or by imaging micro-spectroscopic methods applied to tiny paint chips embedded in resin. The work is undertaken in collaboration with the Rijksmuseum, Mauritshuis and other major museums.

MOLART AT AMOLF

New insights into the maturation of oil paint point to the formation of ionomeric substances, in which metal ions play an important role as binding elements. External forces on the ionomeric structure and intrinsic factors such as the quality of the pigments are major causes of "diseases" in paintings. A severe case is the phenomenon of dissolution of the mineral phases in paint layers, which results in transparent globular masses that appear at the surface as circular protrusions. Comparative imaging FTIR studies in collaboration with the Mauritshuis have shown that fatty acid metal carboxylates are highly concentrated in these protrusions. The composition of precipitating minerals in the metalsoup matrix suggest that the dissolution must be happening under severely basic conditions.

The oxidation and polymerization of oil and egg derived lipids is investigated with ESI-FTMS, MALDIMS, and size exclusion chromatography (SEC). ESI is a very sensitive method for analysis of oxidized triglycerides and phospholipids. MALDIMS demonstrated cross-linked oligomeric lipids up to at least the hexamer. SEC suffered from very strong retention of triglycerides probably due to adsorption to the separation material. Subsequent SEC-DTMS work was therefore inconclusive. The addition of mastic, copaiva balsam and asphalt to drying oil greatly influences the oxidation and cross-linking process during light aging. The native Copaiva balsam first retards but more oxidized derivatives subsequently accelerate the photo-induced oxidation and cross-linking processes of the drying oil. Asphalt strongly retards the photo-oxidation of the oil.

Many organic pigments, both traditional and modern synthetic ones, can be identified using laser desorption ionization methods. Embedding of these pigments in metal and mineral rich paint present many analytical difficulties. One problem investigated is the rapid depletion of pigments by the early laser shots resulting in overwhelming signal from the inorganic fractions, which makes a quantitative approach very difficult. Earth pigments are notoriously difficult to identify in paint. A large number of well defined Kassel and Cologne earth samples have now been analyzed by DTMS and PyGCMS. These fossil wood and leaf materials contain

polymeric and biomarker fractions that could affect the drying of oil paint. A black pigment sample from an early 19th C collection could be identified as asphalt possibly from the Dead Sea. The effects of earth pigments was studied in 25 year old paints made available by the Canadian Conservation Institute in Ottawa. Asphalt has the strongest anti-oxidant effect.

The preparation of indigo for use in 17th C oil paint is a major research topic of MOLART's art historian Van Eikema Hommes. The fate of indigo in paint and the photodegradation processes in paintings are investigated by the AMOLF team using HPLC, MS and imaging FTIR. Natural indigos are very quickly photo-oxidized compared to synthetic indigo. A certain protective effect is provided by uptake in protein prior to inclusion in oil paint. HPLC studies of the photo-oxidation products are underway as a prestudy for HPLC-ESIMS work early next year. Fundamental microspectroscopic imaging (UV-VIS and FTIR) studies are performed to develop a chemical microscopic identification protocol in cross-sections. Indigo can be shown directly in cross-sections with laser desorption ionization MS.

An extensive survey of pigments and media by light microscopy, imaging FTIR and MS has started on paintings by ten different artists from the Oranjezaal in the Royal Palace Huis ten Bosch in The Hague. This is a project in which knowledge acquired by the MOLART team is applied to art historical and art technical studies. This project is an extension of earlier work on the varnishes, the effect of solvent cleaning and wax-resin relining. Systematic studies are performed by Van der Doelen en Speleers on pigments and media to understand relationship between the choice of painting material and artistic expression.

EFFECTS OF LASER CLEANING IN COLLABORATION WITH ART INNOVATION

CREART is a joint research project between several EU countries. At AMOLF, the research is focussed on the effects of laser cleaning on paintings using similar dosimetric systems as developed during an earlier European project (ERA). DTMS and MALDIMS is applied to study the extent of the damage caused by excimer laser exposure (248 nm). The oxidation state of the lipids in the egg tempera paint dosimeters are studied to obtain a measure of the potential damage to the paint. Thermal effects during excimer laser cleaning were studied with a PtSi camera. Only small increases in temperature were observed. Data obtained from laser cleaned dosimeters are with the same systems cleaned in conventional ways with solvents.

INVESTIGATORS : G. van der Doelen, L. Speleers, J. Van den Berg, N. Wyplosz, G. Languri, O. van den Brink, J. van de Weerd, K. Keune, P. Novotna, N. Vermist and T. van Diepen.

TECHNICAL SUPPORT : J.van der Horst, M.C. Duursma and A. Kerkhoff.

J.J. Boon is also professor of biology at the University of Amsterdam

3. STRUCTURE, FUNCTION AND FLOW OF SOFT MATERIALS

Program coordinator: D. Frenkel

Soft materials (polymers, liquid-crystals, colloids, food-stuffs, paints, pharmaceuticals and biomaterials) differ in important respects from 'hard' materials (metals, semiconductors, dielectrics) as a result of the presence of a large number of degrees of freedom that can be excited at room temperature. These degrees of freedom are associated with structural elements of a size much larger than the atomic scale but sufficiently small for thermal fluctuations to be important. Typical for soft materials is the large diversity in properties even for chemically closely related systems. Here, both the conformational freedom and the mesoscopic size of the building blocks play an important role, the former *enabling* the variety, the latter *allowing the control* over their properties. Aside from the large scale of modern functional materials, the endless opportunities for the design of novel materials is manifest in 'living' matter, where energy consuming processes enable the assembly of ever more complex systems.

Within the FOM-wide program *Structure, function and flow of soft materials*, the research at AMOLF concentrates on the following specific aspects of soft materials:

- Properties associated with length scales where fluctuations dominate
- Phenomena that allow the design of novel materials with specific properties
- Structure formation and transport in bio-molecular systems
- Theoretical and numerical tools to model and predict the properties of soft materials
- Maintaining state-of-the-art instrumentation and the development of novel apparatus

The technical infrastructure provided by AMOLF, and partly funded by this FOM-AMOLF program is essential to carry out this research program, which has some heavy instrumental components:

- X-ray scattering - both in-house on a rotating anode spectrometer and at the European Synchrotron Radiation Facility (ESRF) in Grenoble
- Real-space scanning probes: Atomic force microscopy, confocal microscopy and optical manipulation (laser tweezers) play a key role
- Workstations and access to main-frame parallel computers

3.1 COMPUTATIONAL PHYSICS

D. Frenkel

The computational physics research at AMOLF focuses on numerical simulation of classical many-body systems with an emphasis on soft condensed matter. A theme common to much of our numerical work is that it aims towards a better understanding of complex, collective phenomena by studying simple model systems that contain the essential physics of the problem. Parallel to such computer "experiments", we perform numerical simulations of real materials under conditions that are not (yet) accessible to experiment. The main themes of the computational work are the study of the structure, dynamics and phase behavior of (bio)macromolecular systems.

During the past year, we made progress in our studies of polymer crystallization, liquid-crystal formation and colloid dynamics. Below, we briefly review some highlights.

POLYMER CRYSTALLIZATION

Temperature changes during the growth of lamellar polymer crystals give rise to steps on the surface of the crystals. The shape of these steps provide detailed information about the thickness selection mechanism in polymer crystal growth. We performed simulations of such temperature-jump induced steps in the context of our earlier work in which we suggested that polymer crystals tend to select a thickness that is determined by stability conditions, rather than growth velocity. The simulations did indeed reveal that the step profiles can be understood in terms of a simple model for the approach to stable growth. However, at higher temperatures, the profiles also contain information about the spontaneous thickness fluctuations in the crystal.

CRYSTALLIZATION

The range of the attractive potential is of crucial importance for the phase behavior of many colloidal and protein systems. However, it is difficult to compare the range of attraction of systems that have a different functional form for the attraction. We proposed an extension of Van der Waals' law of corresponding states that can be applied to colloidal suspensions that have widely different ranges of attractive interactions. We showed that, for such systems, the "reduced" second virial coefficient is a convenient parameter to quantify the effective range of attraction. This procedure allows us to give a simple definition of the effective range of attraction of potentials with different functional forms. The advantage of this approach is that it allows us to estimate the relative location of the liquid-vapor and solid-fluid coexistence curves exclusively on basis of the knowledge of the pair-potential.

LIQUID CRYSTALS

Recent experiments at the Van 't Hoff laboratory in Utrecht have focused on the phase behavior of hard, disk-like colloids. These experiment confirmed an old numerical prediction, namely that disklike particles with purely repulsive interactions can form a columnar phase (see: D. Frenkel, *Liquid Crystals* 5:929(1989)). However, the phase behavior of the experimental systems is more complicated due to polydispersity of the disks. In addition, addition of non-adsorbing polymer can have a pronounced effect on the phase boundaries. We studied both effects in simulations. We found that when large polymers are added, the disks exhibit a fluid-fluid transition in the isotropic phase. In contrast, small polymers induce demixing in the nematic phase. These phenomena occur both for stiff and flexible polymers. However, quantitatively, there are large

differences. We also studied the phase behavior of two-dimensional lyotropic liquid crystals. Such systems can be prepared experimentally in confined geometries.

The phase behavior was mapped out as a function of the aspect ratio of the particles. For long rods, a 2D nematic phase is observed at high density in which the orientational correlation functions decay algebraically, indicating that the phase does not possess true long range orientational order. The simulation data indicate that the transition from this phase to the low density isotropic phase is continuous, via a Kosterlitz-Thouless disclination unbinding type mechanism, rather than first order. For short rods the nematic phase disappears so that, on expansion, the solid phase undergoes a first order transition directly to an isotropic phase.

Although the latter phase is globally isotropic, we find evidence for strong local positional and orientational correlations between the particles. In this context, we also investigated the effect of vacancies on the melting process in two dimensions. We found that, although the vacancy concentration at melting is quite high (up to 0.5 %), the vacancies appear to have little effect on the location or nature of the melting transition.

ALGORITHMS

An important problem in the mesoscopic modeling of liquids is that the existing dissipative particle dynamics (DPD) schemes are ill suited to treat non-ideal fluids. We showed how, starting from a Van der Waalslike free-energy functional, we are able to design a DPD scheme for non-ideal - even phase separating - liquids.

INVESTIGATORS : N. Kern, M. Alves de Inda, C. Das, S. Auer, S. Pronk, F. Capuani, J. Horbach, M. Noro and M. Bates

D. Frenkel is also professor of chemistry at the Universities of Amsterdam and Utrecht

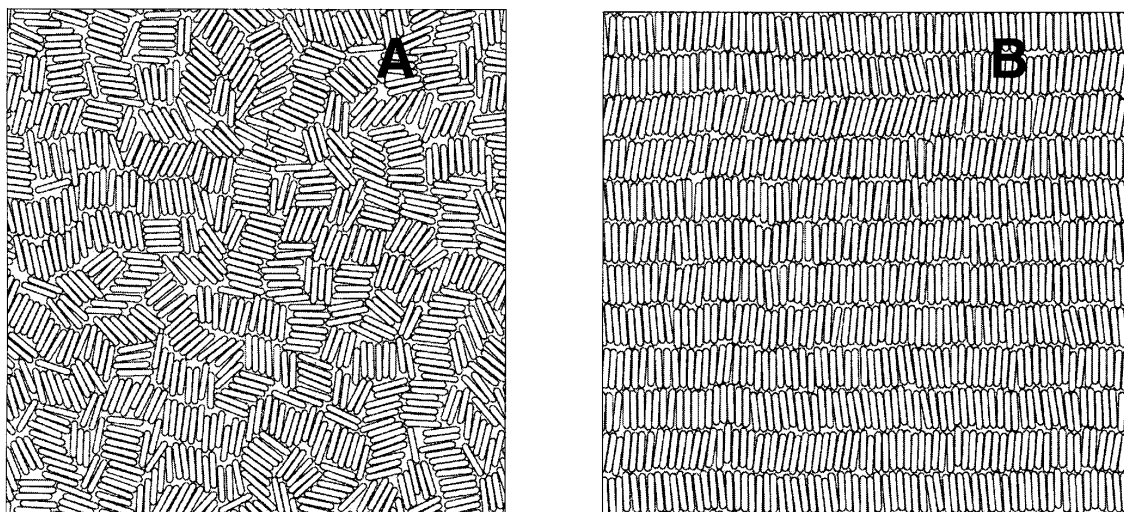


Fig. 1: Structure of the isotropic fluid (A) and solid (B) phases of a two-dimensional system of hard rods with aspect ratio $L/D=5$. Note that the isotropic fluid phase has appreciable local orientational ordering, due to the tendency of the rods to form "stacks". Still, the fluid phase exhibits no long-ranged orientational order.

3.2 BIO-ASSEMBLY AND ORGANIZATION

M. Dogterom

This group focuses on physical processes that contribute to the transport and spatial organization of macromolecular aggregates in living cells. The aim is to unravel, through quantitative experiments under simplified conditions, the physical mechanisms underlying these processes.

Microtubules are rigid tubular structures (diameter 25 nanometer) that self-assemble from tubulin proteins. The assembly of a single microtubule generates pushing forces that are important, for instance, for the motion of chromosomes during cell division. We measure the magnitude of these forces by letting a microtubule polymerize against a microfabricated glass barrier and analyzing the subsequent buckling of the microtubule as a function of time. We find that at high enough polymerization velocities, forces up to 10 piconewton can easily be generated and that the stall force (needed to stop the growth of a single growing microtubule) seems significantly higher. In an attempt to measure the stall force directly we set up an experiment using optical tweezers shown in Fig.1. We also found evidence that the so-called catastrophe rate, the rate at which growing microtubules switch to a state in which they rapidly shrink, is enhanced when a force is applied to the end of a growing microtubule.

In many cells, microtubules are nucleated by one or two microtubule organizing centers forming so called microtubule asters. Polymerization forces such as described above are likely to play a role in the positioning of these asters in the confined geometry of living cells. *In vitro*, a single aster assembled from purified tubulin positions itself near the geometrical center of a microfabricated chamber. We constructed artificial asters by attaching microtubule nucleation sites to silica beads. We find that repositioning (after displacement of an aster from the center using optical tweezers) is only possible when the microtubules switch sufficiently often between growing and shrinking states. When microtubules become too long due to a lack of switching events, they buckle, grow around the edges of the chamber and no positioning occurs (see Fig. 2).

In plant cells microtubules are nucleated in a more random fashion, and ordered microtubule arrays form just below the cell membrane. In collaboration with the group of B.M. Mulder and the groups of A.M.E. Emons and D. Gadella from the University of Wageningen we investigate the possible mechanisms by which these ordered arrays form. Through *in vitro* experiments and computer simulations (in collaboration with M. Dijkstra from the University of Utrecht) we study how polydisperse rods (microtubules) organize in quasi two-dimensional systems. The simulations predict a transition to an ordered (aligned) phase at volume fractions in the range of the *in vitro* experiments.

Membrane structures in living cells such as the Endoplasmic Reticulum and the Golgi apparatus show morphologies that differ dramatically from equilibrium lipid bilayer systems. In part, these morphologies are believed to be due to the interaction of lipid bilayers with active components such as molecular motors and dynamic microtubules. To study the morphological changes that may arise due to such interactions we have started to develop an *in vitro* model system that allows us to link lipid vesicles to a network of microtubules through active motor molecules.

Optical trapping techniques can be used to measure forces on the order of several (tens) of piconewton using

micron-sized colloids. Using colloids with a high index of refraction should in principle allow for the measurement of larger forces, provided that trapping is not impaired by scattering forces in the direction parallel to the beam. In collaboration with the group of A. van Blaaderen we have investigated the trapping capabilities of core-shell particles that consist of a high index ($n \sim 2$) zincsulfide core and a silica shell. While it is clear that stronger trapping occurs in the directions perpendicular to the direction of the laser beam, the particles are readily displaced from the trap in the parallel direction. To make use of the stronger trapping capabilities of these particles, double optical tweezers with counter-propagating beams are being set up.

INVESTIGATORS : M. Cosentino-Lagomarsino, C. Faivre, M.E. Janson, G. Koster and W. Roos

TECHNICAL SUPPORT : A. van der Horst and M. van den Boer

M. Dogterom is also professor of physics at the University of Leiden.

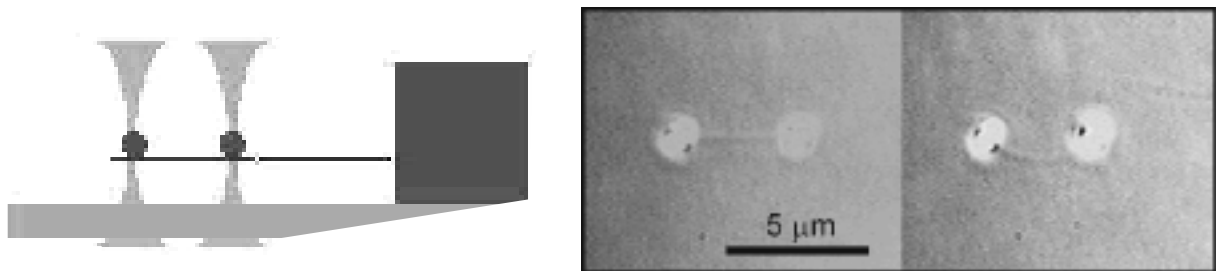


Fig. 1: Schematic representation (left) of an experiment designed to measure the stall force of growing microtubules. Two colloids are attached to a microtubule seed that acts as a template for microtubule growth. When the beads are trapped in double optical tweezers (used on the right to bend a microtubule seed) the growing microtubule end can be brought into contact with a rigid barrier. Displacement of a bead with respect to the center of a trap will allow for the measurement of the force needed to stall the growing microtubule.

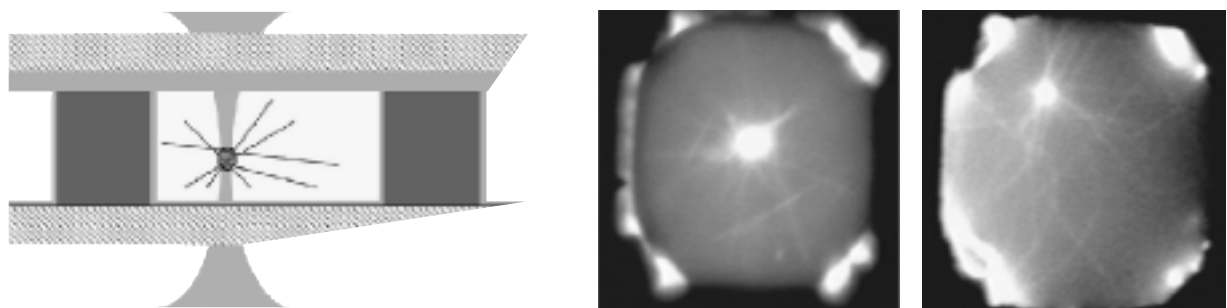


Fig. 2: Optical tweezers are used to manipulate the (initial) position of an artificial microtubule-organizing center in a microfabricated chamber (left, schematic side-view). After release of the center dynamic microtubules allow for the positioning of the aster (left fluorescent image, top view). When the microtubules become too long, they bend and (re)positioning no longer occurs (right image). Chamber size is 20 μm , depth 3 μm .

3.3 ORDER/DISORDER IN SOFT MATTER

W.H. de Jeu

The objective of the group is to study and control the ordering of soft materials using X-ray methods and optical and atomic force microscopy. Block copolymer films are used to obtain nanostructures and to study polymer crystallization in confined geometries. Smectic membranes are investigated as model systems of low-dimensional ordering.

In a diblock copolymer ordering arises due to the difference in chemical properties of the A- and B-blocks ("surfactant"-like behavior). For about equal amounts of A and B this can lead to microphase separation into a lamellar structure. These randomly oriented lamellar microdomains become macroscopic under the influence of surfaces. We exploit additional ordering principles within one of the blocks to manipulate and control the generic block copolymer structures in films ("tandem" interactions). An example is the incorporation of comb-shaped LC polymers into one of the blocks. In one case a strong anchoring of the smectic layers is found parallel to both the substrate and the air. As the block interfaces remain orthogonal to the smectic layers as in the bulk, they are now *perpendicular* to the substrate. Attempts are made to align the resulting nanostructures macroscopically uniformly using an additional electric field.

The application of external "fields" like pressure, shear or specific boundary conditions, gives a means to influence and possibly control the pathways to the crystallization of polymers. We have used uniform diblock copolymer films to provide precise control of the boundary conditions for the crystallization of one of the blocks. In contrast to homopolymers, in diblocks equilibrium chain folding can be achieved. We crystallized the PEO-blocks of symmetrical PEO-PB_n diblock copolymer films isothermally from the ordered melt. An increase is observed in the lamellar thickness of the PEO-blocks, which can be accommodated by the rubbery (flexible) walls of the PB_n blocks. As the density of PEO increases upon crystallization, this effect is accompanied by a contraction in the lateral direction, leading to the formation of holes and cracks in the films. Depending on the crystallization temperature changes are observed from integer to half-integer ratios of the folded to the fully extended chain.

X-ray studies of the bulk crystallization of several polymers have been reported indicating the occurrence of an induction period from the SAXS intensities, which precedes the crystallization as observed in WAXS. These results have been rationalized via a coupling of density and chain conformation. Orientational ordering of the chains during shear leads to a strong increase in the nucleation and growth of crystals, which is qualitatively in agreement with this picture. In order to start investigations of shear-induced ordering in crystallisable polymer melts, we have built a versatile small-angle scattering set-up supplied with a sample cell combining accurate temperature control with the possibility to apply shear. This will provide a home base for the preparation of more demanding time-resolved measurements at synchrotron sources.

In liquid crystals a free surface may stabilize a higher ordered phase. An extraordinary example is found in smectic membranes of the compound abbreviated as 4O.8, which shows with decreasing temperature layer-by-layer crystallization starting at the film surfaces. Moreover, this transition from a smectic-A (SmA) phase with liquid layers into a crystalline B phase (CrB) is mediated via a surface induced hexatic smectic-B phase (SmB) not observed in the bulk. Hence this behavior of a single top layer is a good model of a two-

dimensional Kosterlitz-Thouless transition. This process has been investigated by grazing incidence x-ray diffraction at beamline ID10B at ESRF (Grenoble, France). The incident angle was set at about twice the critical one. As a consequence the diffracted intensity also contains information about the liquid structure of the inner layers. In the SmA phase of an 8 layer film a broad liquid peak is observed as expected. The transition to hexatic SmB with limited positional order (6 inner liquid layer and 2 hexatic top layers) was found to be gradual. The final CrB structure is reached abruptly within our temperature resolution of about 0.1°C. It shows a sharp resolution limited peak from the two crystalline top layers with underneath still the liquid peak from the 6 inner layers.

The reduced dimensionality of smectic liquid crystals leads to strong thermal fluctuations of these layers. As a consequence their positional ordering is not truly long-range: the mean-square displacement of the layers diverges with the sample size (Landau-Peierls instability). Due to these properties there is a profound interest in smectic membranes, which have a controlled number of layers. Their dynamics has been studied using X-ray photon correlation spectroscopy using coherent X-rays at beamline ID10A at ESRF (Grenoble). The theoretical description predicts various modes of which the basic surface one decays with a time constant $\tau = D/(2\gamma)$. Here γ is the viscosity associated with shear of the liquid layers, D the film thickness and γ the surface tension. For this relatively slow mode $\tau/\mu\text{s}$ is of the same order as $D/\mu\text{m}$. Using standard 8 keV X-rays we observed relaxation times in the submicrosecond range. For these relatively thin Sm-A films we resolved both an oscillatory and a damping behavior of the intensity-intensity correlation function. In agreement with recent theory this indicates that the inertial term in the dynamic equations cannot be disregarded anymore for thin films.

INVESTIGATORS : A. Fera, R. Kleppinger, D. Lambrea, L. Li, R. Opitz, B. Ostrovskii (guest), D. Sentenac, Y. Serero, A.N. Shalaginov (guest) and I. Sikharulidze

TECHNICAL SUPPORT : E. Prins.

W.H. de Jeu is also professor of polymer physics at the Eindhoven University of Technology.

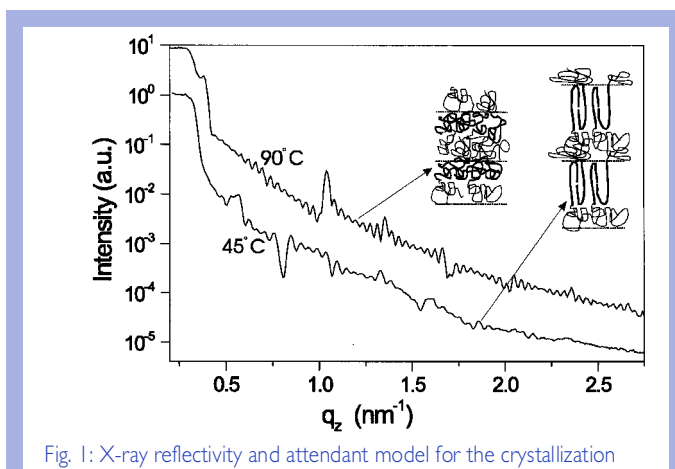


Fig. 1: X-ray reflectivity and attendant model for the crystallization of PEO-blocks in a 6 layer diblock PEO-PB_n film at 45°C.

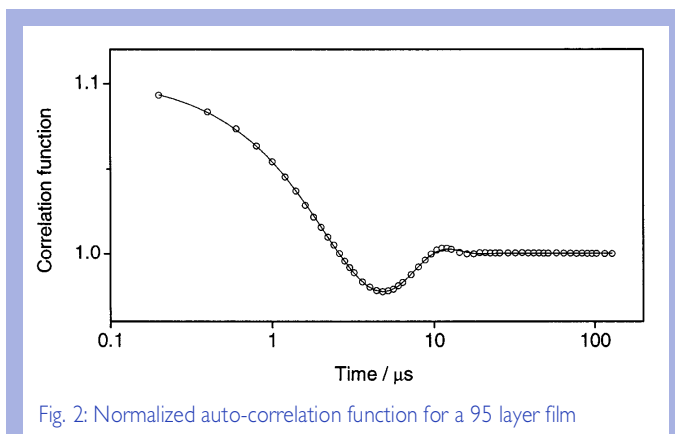


Fig. 2: Normalized auto-correlation function for a 95 layer film (thickness 0.27 μm) in the Sm-A phase of 4O.8; the solid line is a fit to an exponential with a sinusoidal amplitude.

3.4 THEORY OF COMPLEX FLUIDS

B.M. Mulder

The aim of the Theory of Complex Fluids is to understand the individual and collective behavior of (bio)macromolecules using the techniques of statistical mechanics. The work is increasingly focused on the description of components of the living cell.

Colloidal crystallization is currently an active area of research, driven by the potential for applications in optical materials with tailor-made properties. A new theoretical approach to crystallization, the so-called Fundamental Measure Theory, promises a new level of quantitative modeling in this area. We have tested this theory on arguably the simplest "caricature" of a colloidal fluid: a system of parallel-aligned hard cubes. Using a combination of theory and simulation we have probed several aspects of the crystallization transition in this system, which interestingly enough is known to be continuous. In contrast with earlier predictions, we give strong evidence that the transition belongs to the Heisenberg universality class. Moreover, we show that the crystalline state is stable with respect to columnar fluctuations, a non-trivial fact as the free-energy of the columnar- and the crystalline state are equal in leading order in the density as one approaches close packing.

In collaboration with the group of M. Dogterom, we have continued our work on the force production of growing microtubules. We have built up a full picture of the workings of the so-called multi-filament Brownian ratchet model. Both stochastic simulations and analytical theory have been employed to show that, in spite of earlier suggestions in the literature, this type of model obeys simple thermodynamic rules for determining the maximum force that can be produced. We are also focusing on the full force-velocity curve in order to make contact with the experimental results, which presently are only available in the regime of loading forces < 5 pN. We have analyzed how the force-velocity curve is influenced by the shift in initial position between the neighboring protofilaments that make up the microtubule. We have also addressed an implicit weakness of models with independently growing protofilaments, by explicitly considering the role of lateral interactions between the monomers of neighboring protofilaments.

Other topics that are being pursued in the group are:

- Theoretical predictions of the phase behavior of liquid crystalline polymeric materials on the basis of mesoscale molecular models that take into account the molecular topology, the relative flexibility of distinct parts of the molecule and the interactions between different molecular components.
- Non-sequence specific models for the structure and mechanical properties of DNA including the influence of effective interactions induced between neighboring base pairs by their hydrophobic nature and the steric constraints imposed by their size and their interconnection through the sugar-phosphate backbone.
- Understanding the cytoskeletal structure of fully grown and dividing plant cells, employing models of semi-flexible polymers in confined geometries in the presence of active binding agents. The main goal of this work, which is carried out in collaboration with biochemists and plant cell biologists from Wageningen University, is an understanding of the dramatic rearrangement of the cortical microtubule network into the so-called pre-prophase band just before cell division.
- Construction of physical models for the expanding cell surface in tip growing plant cells, which grow by the localized addition of both cell membrane and wall material through exocytosis of Golgi vesicles. We aim to

include the influence of the "aging" of the wall matrix material on the mechanical properties of the cell surface, a major determinant in tip morphogenesis.

INVESTIGATORS : P. Wessels, C. Tanase and A. Moskalenko

Fig.1: Snapshots of a constant pressure Monte Carlo simulation of parallel hard cubes in the fluid phase at reduced pressure $P=2.8$ in the fluid phase (left) and at pressure $P=18$ in the solid phase (right).

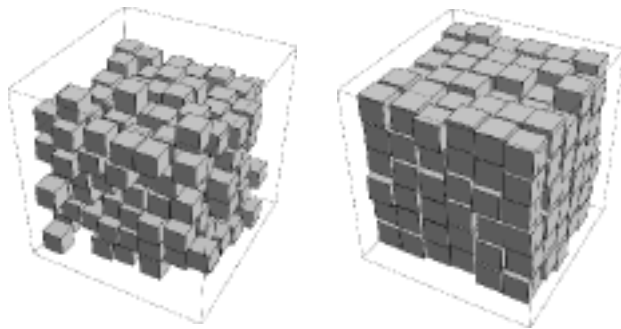


Fig. 2: Model of a multi- protofilament microtubule growing against a diffusing barrier loaded by a force F .

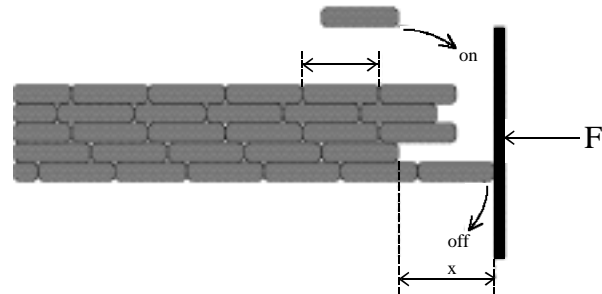
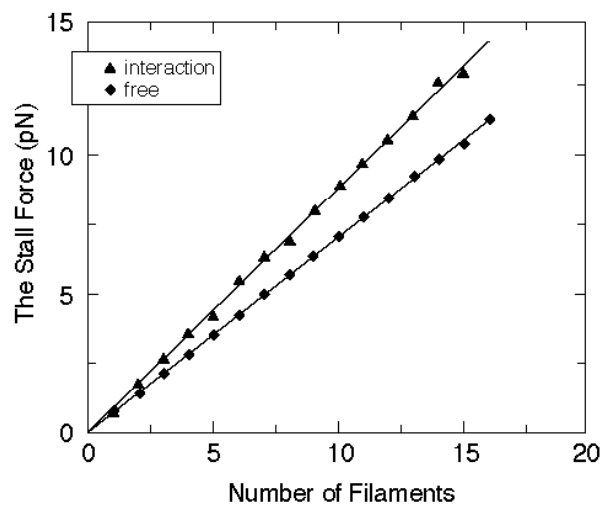


Fig. 3: The stall force as a function of the number N of protofilaments obtained from simulations both in the interacting (triangles) and the non-interacting (circles) case, verifying the linear scaling predicted by thermodynamical arguments.



3.5 COLLOIDAL MATERIALS

A. van Blaaderen

The emphasis of this group is on the quantitative 3D real-space analysis and manipulation of colloidal structures and processes. Motivation comes both from the use of monodisperse colloids as a condensed matter model system, and from their use in applications like photonic crystals and electro-rheological fluids.

Using colloidal epitaxy, directed colloidal crystallization by a template, we have grown the first HCP colloidal crystals (see figure 1). These crystals are metastable and would not have grown without the template, also depicted in the figure. We have also shown that it is now possible to design any close packed stacking sequence and direct the crystal growth by a template. In addition to manipulating colloidal crystallization for particles with a "hard" potential, we have successfully induced crystallization for particles with a double layer of the same order as the particle size. Crystallization of an FCC structure was induced with a template of charged lines in the (110) crystal growth direction. Complete (110) registry was still found 20 layers above the template. Moreover, colloidal epitaxy can direct crystallization with controlled drying as well. With this method that is important for photonic crystal studies, thin colloidal crystals can be grown. Templates for colloidal epitaxy were also made by sticking colloids to an oppositely charged wall with optical tweezers.

Colloidal particles in a gravitational field form an equilibrium height distribution in which osmotic pressure and density differences are balanced. We have found that there is a discontinuous and simultaneous freezing of the first two layers as indicated by the radial distribution function and a bond order correlation function, in accordance with recent computer simulations and density functional calculations.

If a dispersion of uncharged colloidal spheres is placed in a (uniform) electric field the dielectric constant difference between particles and solvent creates dipolar interaction potentials between the spheres. We have found a new model system in which to study the effects of the induced anisotropic dipolar interactions. With PMMA-shell silica-core dispersed in a mixture of organic solvents both the density and refractive index can be matched. In addition a dipolar response to an electric field was found to be superimposed on a very long-ranged screened coulomb potential. Because of the interplay between these two long-range and soft potentials a very rich phase diagram is present, which is still being explored.

We found a layer-by-layer transition of a face centered cubic crystal into a body centered tetragonal (BCT) crystal, when a low frequency (~ MHz) electric field is applied to a dispersion of spheres with the field perpendicular to gravity. As a function of field strength, first the top layers go to BCT, then the subsequent layers. Crystallization in the presence of an electric field that is perpendicular to gravity allows one also to create very large, mm size, FCC single crystals (see figure 2).

In "proof of principle experiments" we have demonstrated the manipulation of multiple colloidal tracer particles with a high-index core by time-shared optical tweezers in a concentrated dispersion of fluorescent core-shell colloids that were index matched. Both the tracer particles and the fluorescent particles could be imaged simultaneously with reflection and fluorescence confocal microscopy. In addition, particle layers above and below the trapping plane could be imaged as well. A start has been made to extend the present set up in such a way that the confocal imaging can be performed through an independent lens allowing for

even greater flexibility of manipulation and analysis.

Real-space measurements on the hard-sphere like PMMA-shell silica-core particles, which are both density and index matched, have resumed. Our first findings on dynamic inhomogeneities close to the glass transition were published in Science.

INVESTIGATORS AMOLF: J.P. Hoogenboom, K.P. Velikov, A. Yethiraj, D.L.J. Vossen, P. Vergeer and A. Wouterse

INVESTIGATORS UTRECHT UNIVERSITY : M. Dijkstra, A. Imhof, Ch. Graf, A. Moroz, Ch. Christova, C.M. van Kats and J.H.J. Thijssen

TECHNICAL SUPPORT : A. van der Horst (AMOLF) and C. Wisman (Utrecht)
A. van Blaaderen is also professor of physics at the University of Utrecht.

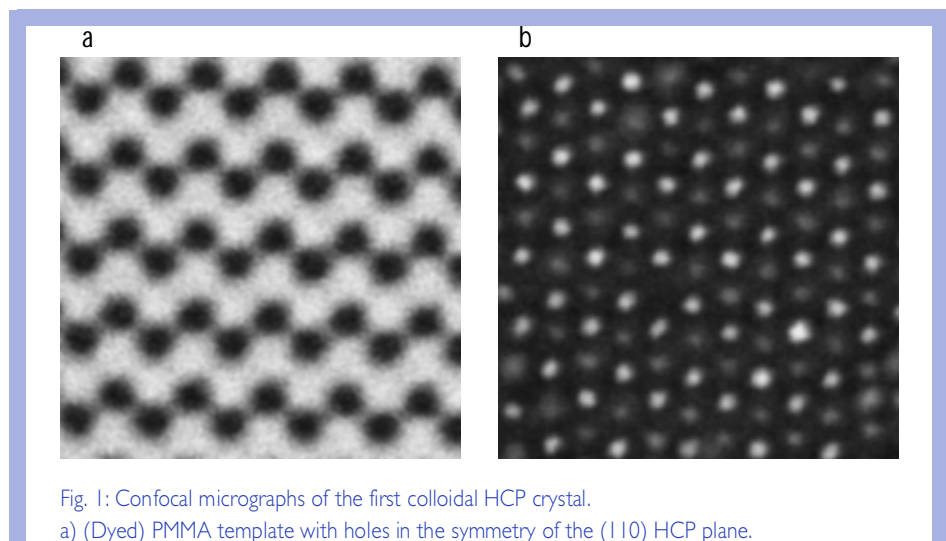


Fig. 1: Confocal micrographs of the first colloidal HCP crystal.
a) (Dyed) PMMA template with holes in the symmetry of the (110) HCP plane.
b) 8th (and vaguely 7th) layer of the HCP crystal above the template.
Sphere diameter 1.4 μm , fluorescent core diameter 385 nm.

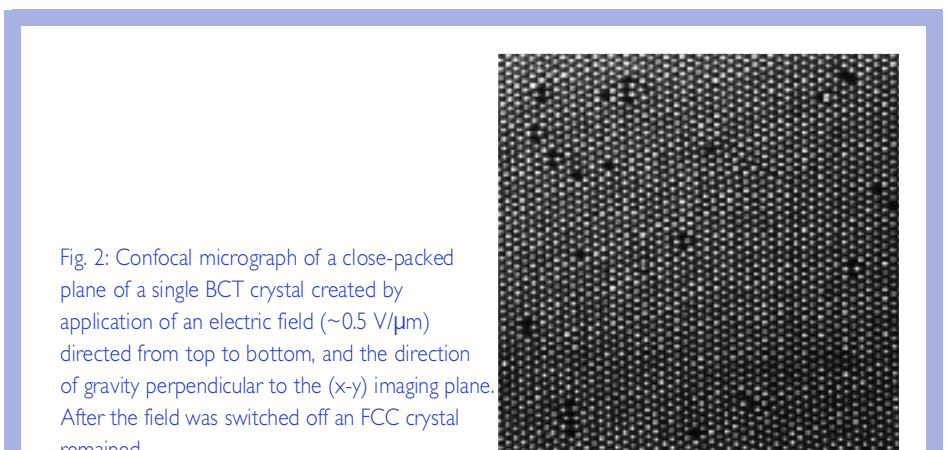


Fig. 2: Confocal micrograph of a close-packed plane of a single BCT crystal created by application of an electric field ($\sim 0.5 \text{ V}/\mu\text{m}$) directed from top to bottom, and the direction of gravity perpendicular to the (x-y) imaging plane. After the field was switched off an FCC crystal remained.

4. NANOSTRUCTURED OPTO-ELECTRONIC MATERIALS

Program coordinator: A. Polman

This program concerns research on materials and physical phenomena in novel photonic structures and materials. It involves thin-film integrated photonic materials made using atomic and molecular scale engineering techniques, as well as colloidal systems. The control of optical modes and spontaneous emission is studied in two- and three-dimensional photonic band gap structures. Linear and non-linear optical phenomena are studied in planar waveguides and colloidal crystals doped with rare-earth ions, dye molecules, and semiconductor/metallic nanocrystals. These studies are complemented with theoretical studies of photonic band gap phenomena and non-linear photonic systems. This research program involves fundamental and strategic technological research, with the emphasis on new physical phenomena and materials. In many cases, the relation with a possible application is kept in mind and knowledge transfer to industry is actively explored.

4.1 OPTO-ELECTRONIC MATERIALS

A. Polman

This group focuses on the design and fabrication of novel opto-electronic materials using atomic-scale engineering techniques. The aim is to achieve extreme control over the propagation of guided optical modes as well as spontaneous emission in thin-film photonic materials.

Polymers are finding more and more applications in photonic integrated circuits. We have studied the incorporation of perfluorinated polymer waveguides with Nd-doped lissamine-sensitized organic complexes. Such a material may be used to fabricate an optical amplifier operating at 1.3 μm . The lissamine sensitizer can be excited optically whereupon rapid intersystem crossing takes place, followed by energy transfer to Nd. We have also developed light-emitting diode structures doped with these organic complexes, and found evidence for electrical excitation of the Nd. The lissamine sensitizer plays a crucial role in mediating the energy transfer from the polymer excitonic system to the Nd 4f shell.

An alternative method to dope a polymer waveguide with optically active rare earth ions is by using a nanocomposit structure, in which rare-earth doped SiO_2 nano-colloids are embedded. Erbium-doped silica colloids show very high luminescence quantum efficiency. Optical gain calculations predict promising optical gain in such waveguides. Er-doped colloids will also find applications in three-dimensional photonic crystals made using self-assembly techniques (see section 4.3). We also continued experiments on the fabrication of anisotropic colloidal particles as well as rare-earth doping of ZnS colloids using ion irradiation techniques.

A novel sensitization concept, involving Er-doped SiO_2 films co-doped with Si nanocrystals, was further developed. We found evidence for strong coupling between the nanocrystal excitonic state and the Er^{3+} intra-4f levels. This concept enables the pumping of rare-earth doped amplifiers using a broad band pump source. Measurements on channel waveguides support our model that, due to Auger quenching to free carriers, no more than one Er ion can be excited per nanocrystal. Experiments on cerium co-doped Er-doped Y_2O_3 waveguides showed that Ce can selectively quench the population of the $^4I_{11/2}$ level in Er^{3+} . This quenching effect can enhance the 980-nm-pump efficiency of Er-doped amplifiers and can reduce the detrimental effect of cooperative upconversion on the optical gain. Furthermore, detailed calculations were made of the optimum design of a miniature Er-doped optical amplifier co-doped with Yb as a sensitizer.

Silicon is an excellent optical waveguide material as it is transparent at 1.5 μm . We have doped Si with Er and studied the energy backtransfer between excited Er and the Si electronic system. We found that the internal backtransfer quantum efficiency is as high as 70 % at room temperature. Channel waveguides were made and serve as a miniature infrared detector showing a room-temperature photocurrent spectrum peaking at 1.5 μm . Limiting effects were identified, and are due to the metal contacts that couple to the evanescent waveguide mode, and absorption by free carriers due to ionized Er and the p- and n-type dopants around the junction inside the waveguide mode.

Two-dimensional Si-based photonic crystals were made using high-resolution lithography and reactive ion etching techniques. To achieve optical confinement in the third dimension the top 2 μm of the structure was amorphized by ion irradiation. We found that amorphous silicon is an excellent waveguide materials with

optical losses at 1.5 μm of 70 cm^{-1} , quite tolerable in a micron-sized photonic crystal structure. Two wet-chemical methods to dope these Si photonic crystals with optical probe ions were developed: one using tetraethoxysilane, ethanol, water and ammonia that coats a thin silica film doped with a luminescent eosin dye onto the Si pillars, and one using ErCl_3 in ethanol, that, if combined with the proper annealing and oxidation treatments, adds erbium to the Si pillars. Measurements on the spontaneous emission of Er in these structures are underway.

Three-dimensional Si photonic crystals were doped with Er in a collaboration with Sandia National Labs. These "wood-pile" type structures have a full 3-dimensional gap centered around 1.5 μm and were implanted with Er. The broad defect-related luminescence signal is suppressed over the full width of the stopgap. In addition, the spontaneous emission rate of Er is reduced. This is the first demonstration of effects on spontaneous emission at the important telecommunication wavelength of 1.5 μm in a three-dimensional photonic crystal with a full bandgap.

INVESTIGATORS : P.G. Kik, L.H. Slooff, M.J.A. de Dood, Ch. Strohhöfer, T. van Dillen, H. Isshiki and M. Hensen

TECHNICAL SUPPORT : J. Derks and J. ter Beek

A. Polman is also professor of physics at the University of Utrecht.

Fig. 1: Schematic of an Er-doped Si infrared waveguide detector. A photocurrent is generated because optically excited Er ions transfer energy to the Si electronic system at an efficiency of 70 %.

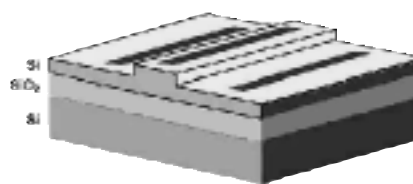


Fig. 2: Optical emission and absorption spectra of polymer films doped with a lissamine-sensitized Nd complex. A polymer light-emitting diode operating at 1.5 μm was made

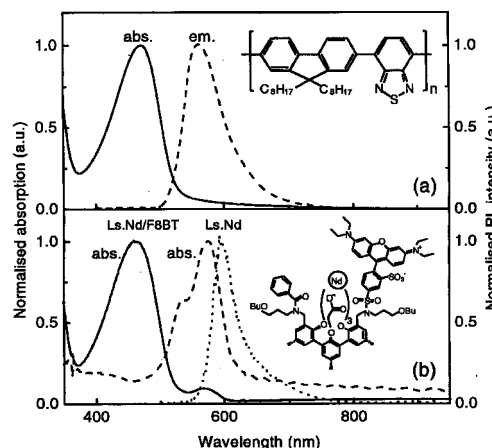
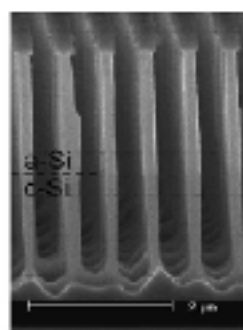


Fig. 3: Two-dimensional Si photonic crystal with a bandgap centered around 1.5 μm . To confine light in the third dimension, the refractive index of the top section of the pillars is increased by amorphization.



4.2 PHOTONIC MATERIALS THEORY

A. Tip

A central issue is the study of Maxwell's equations for periodic structures such as photonic crystals. Topics under consideration are their quantization (relevant for the decay of embedded atoms) and the modifications that are needed if absorption takes place.

An early example of a modification of vacuum electrodynamics is "cavity electrodynamics", the situation where the fields are confined inside a metallic cavity. This alters the structure of the electrodynamic field modes with the consequence that the electromagnetic decay properties of an atom in a cavity differ from their free space counterparts. Quite dramatic changes can be obtained by using more sophisticated structures, such as photonic crystals with a bandgap. A photonic crystal is a dielectric structure with spatial periodicity, leading to a band structure of its spectrum of eigenmodes. Under favorable conditions (large contrasts in the electric permeability) it can have one or more bandgaps, thus inhibiting electromagnetic decay by single photon emission of atoms with a transition frequency inside such a gap. Then there are no field modes to carry away the atomic excitation energy and it remains in its excited state, until it decays by multiple phonon emission or some other process.

A few years ago we started with photonic bandgap calculations for two and three dimensional systems using an adaptation of the KKR-method of solid state physics. That method is tailor-made for the electromagnetic situation (typically nonoverlapping spheres on lattice sites), where we are always dealing with nonoverlapping scattering centers in a homogeneous background. However, the vector nature of the electromagnetic fields makes the formalism a good deal more complicated than in the solid state case. It has turned out that a large contrast in ϵ between scatterer and background is required to obtain appreciable bandgaps in the optical region with the case of low ϵ scatterers in a high ϵ background as the most favorable one. Actually available materials set a severe restriction on what can be achieved along these lines.

The situation improves significantly if Drude-type metallic spheres are used. They behave as lossy dielectrics with the real part $\text{Re}(\epsilon(\omega))$ of $\epsilon(\omega)$ ranging through a large interval, including negative values, as ω runs through the optical frequency range. Disregarding absorption, a large bandgap is found at frequencies where the absorption is small, thus *a posteriori* justifying its neglect.

However, the presence of appreciable absorption raises a number of fundamental questions:

- What happens to the band structure in the absorptive case and how does one define bandgaps?
- How does one now quantize the electromagnetic fields (needed to describe atomic decay)?
- What can be said about the absorption per unit length in a given direction as an electromagnetic wave travels through a medium containing absorptive scatterers?

During the past year we found a satisfactory answer to a). We developed a theory where it is shown that the bands change into areas in the complex plane and we gave a satisfactory definition of a bandgap which reduces to the common one in the nonabsorptive case. Maybe somewhat surprisingly, bandgaps do not occur if absorption takes place. This can be understood by realizing that gaps depend on delicate interference properties after scattering from a large amount of scatterers. However, if most of a traveling wave is already absorbed before reaching distant scatterers it is clear that gap formation can be jeopardized. As a result atoms can now be de-excited. Their energy is no longer transported to infinity 'on the back of an electromagnetic wave' but

is absorbed locally instead. Problem b) was already solved a few years ago. In two subsequent issues of PRA two different theories, the first by the Jena group and the second by us, were presented, which dealt with this problem. In a joint paper with the Jena group we recently showed that these theories are in fact equivalent. We also started band structure calculations for a two-dimensional FCC lattice with Drude cylinders on the lattice sites. Our preliminary results show that indeed areas in the complex plane emerge. We now are preparing to tackle problem c). For this we have to calculate the Green's function associated with the Helmholtz equation. This involves more complicated calculations than for the band structure but is in fact more fundamental. Not only the absorption per unit length but also radiative atomic decay rates are given in terms of it.

INVESTIGATORS : H. van der Lem

Fig. 1: The real part $\text{Re}(\epsilon)$ and imaginary part $\text{Im}(\epsilon)$ of the electric permeability as a function of frequency for a Drude metal. Note that $\text{Re}(\epsilon)$ changes from negative to positive values.

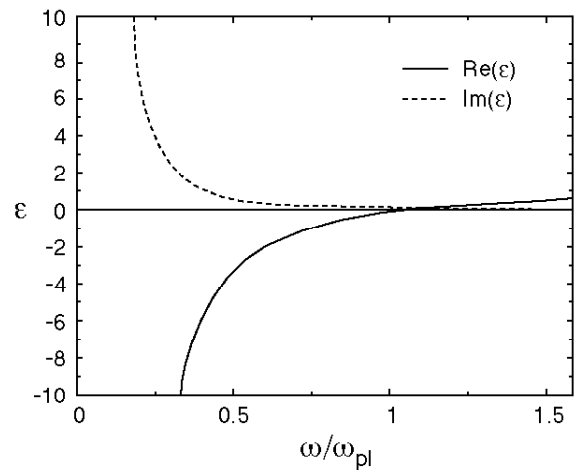
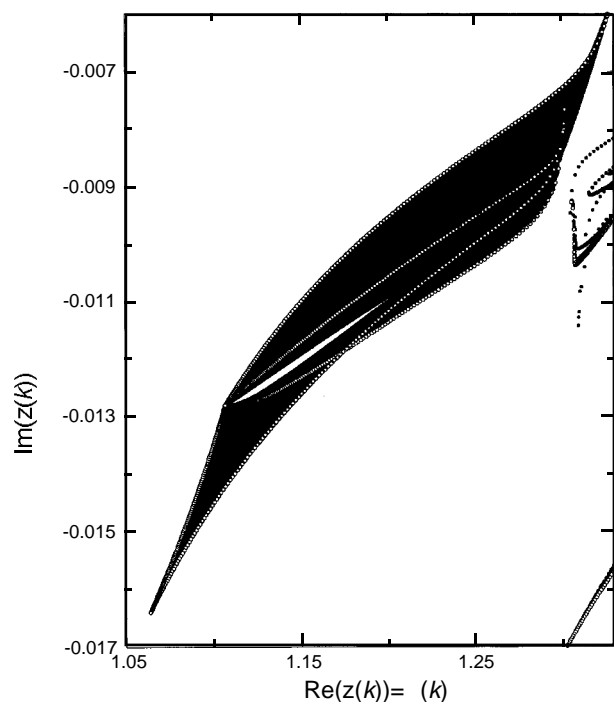


Fig. 2: Detail of the band structure for a two-dimensional FCC Drude lattice. Note the presence of a hole in an otherwise filled area



4.3 COLLOIDAL PHOTONIC MATERIALS

A. van Blaaderen

The emphasis of this group is on the quantitative 3D real-space analysis and manipulation of colloidal structures and processes. Motivation comes both from the use of monodisperse colloids as a condensed matter model system, and from their use in applications like photonic crystals and electro-rheological fluids. Structural aspects of this work are described in 3.5.

We have grown thin FCC photonic crystals through a controlled drying procedure of colloidal particles with high-index-ZnS core-shell morphology and performed transmission measurements on these crystals. As predicted by theory particles with a ZnS core and a silica shell with a core-radius/total-radius ~ 0.7 have a higher (111) relative stop-gap-width than pure high index particles with the same total radius. The gap width is even higher than for pure ZnS shells (i.e., without silica inside).

With ion implantation Er ions were made to luminesce inside individual ZnS-core silica-shell colloids with lifetimes in the ms range. A start has been made to try to incorporate Er inside silica colloidal particles through a wet chemical route.

Theory has shown in the last few years that it may be possible to obtain a complete photonic band gap in the visible using metallo-dielectric structures. In order to test these predictions we successfully modified a recent synthesis route for gold particles to that of silver. We obtained particles with radii covering the colloidal range. Although the polydispersity of the particles was too high to obtain close packed crystals, we did obtain crystals when the filling fraction of the crystals was relatively low (see Fig. 1). Reflection measurements on an amorphous packing of these spheres already showed significant ($\sim 20\%$) changes in reflectivity. We have also started the synthesis of metallo-dielectric spheres by growing gold layers around silica and silica on gold spheres. With ion irradiation these spheres could be deformed into core-shell ellipsoids.

We have extended the method of controlled drying to make thin photonic crystals of binary crystals. If a correct size ratio is chosen, close to that for bulk crystallization of binary crystals, AB_2 crystals can be grown in a layer-by-layer fashion (Fig. 2).

INVESTIGATORS AMOLF: J.P. Hoogenboom, K.P. Velikov, A. Yethiraj, D.L.J. Vossen, P. Vergeer and A. Wouterse

INVESTIGATORS UTRECHT UNIVERSITY : M. Dijkstra, A. Imhof, Ch. Graf, A. Moroz, Ch. Christova, C.M. van Kats and J.H.J. Thijssen

TECHNICAL SUPPORT : A. van der Horst (AMOLF) and C.J. Wisman (Utrecht)
A. van Blaaderen is also professor of physics at the University of Utrecht.

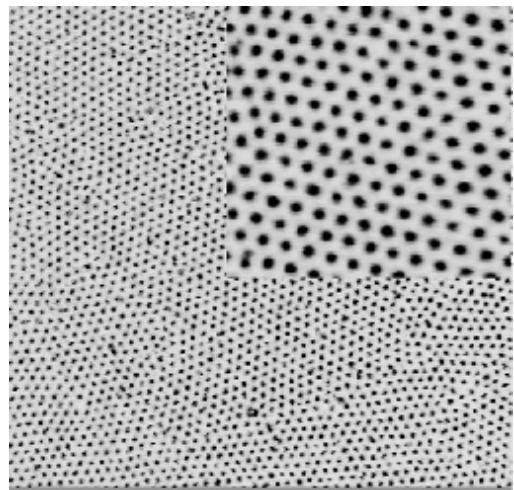


Fig. 1: Reflection confocal microscopy pictures of an (111) FCC colloidal crystal plane against the glass container wall of Ag spheres with an inter particle distance of 900 nm (radius 258 nm).

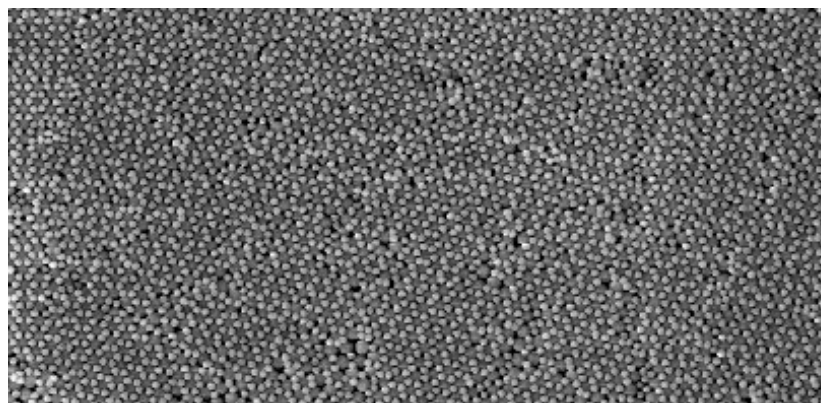


Fig. 2: SEM pictures of: two layers of silica particles with size ratio 0.60 (larger sphere radius 202 nm) deposited by a controlled layer-by-layer drying process. The two layers form the start of an AB₂ crystal.

5. TRANSITION PROGRAM

Program coordinator: J.T.M. Walraven

The AMOLF Transition Program consists of research activities which are not embedded in one of the four main programs of the institute. Presently, the transition program bundles the work in the groups Quantum Gases and Molecular Beams.

5.1 QUANTUM GASES

J.T.M. Walraven

This group investigates many-body and atom-optical properties of dilute ultra-cold gases confined in magnetic traps. The aim is to gain insight in the condensed matter behavior of dilute Bose-Einstein condensed gases and to push the level of control over such gases to new extremes.

The concept of degenerate quantum behavior in gases, in particular the phenomenon of Bose-Einstein condensation (BEC), has its origin in the quantum mechanical analogy between matter waves and light waves. As the temperature of a gas drops, the de Broglie wavelength of the atoms increases. Once the thermal wavelength approaches the mean interparticle separation, the quantummechanical indistinguishability of atoms leads to a noticeable enhancement of the occupation of already occupied modes of propagation. Bose gases undergo the BEC transition which results in a macroscopic occupation of the ground state (condensate formation). BEC manifests itself as a phase transition in which the properties of a gas change dramatically. Above the transition temperature T_c , the gas behaves normal, i.e., as a collection of atoms with a statistical distribution of velocities. Below T_c this classical behavior changes to the unique behavior of the wavefunction of a macroscopically occupied single quantum state. Dilute Bose-condensed gases allow theoretical description of many-body quantum behavior from first principles. On the experimental side, trapped gaseous samples are exceptionally well isolated from the environment. This enables the virtual elimination of outside disturbances when investigating macroscopic quantum effects. Moreover the alkalis are well matched to the powerful optical precision methods of atomic physics. This combination of experimental and theoretical 'accessibility' of BEC in ultra-cold gases allows one to get a good insight in the remarkable many-body properties of these systems.

Our experimental research is focused on the investigation of Bose-Einstein condensates in a system with a large number of ^{87}Rb atoms. The aim is to explore the onset of hydrodynamic behavior, which is expected to occur when the mean free path of the atoms becomes less than the size of the gas cloud. Under these conditions the transport phenomena change drastically and this is known to have important consequences for the properties of the gas. We investigated the implications of this dense regime for the creation of Bose-Einstein condensates by rf-evaporative cooling. We found that it is possible to produce condensates with densities up to $1.7 \times 10^{15} \text{ cm}^{-3}$ at a temperature of 530 nK. As expected, at these densities the gas clouds are already collisionally thick. In contrast to low density samples, at high densities special attention has to be paid to the evaporation procedure, in particular with regard to density related heating and loss mechanisms. We found direct evidence for the presumed existence of 'Oort clouds' of trapped atoms surrounding the cold sample (see Fig. 1). As the density of the Oort cloud is very low it cannot be observed by the usual absorption imaging. By recapturing the cloud into a magneto-optical trap we could establish that in our case the Oort cloud can consist of up to a million atoms with energies up to several millikelvin. We investigated how the occupation of the Oort cloud depends on the evaporation procedure and how its presence can be shielded from the cold sample by an rf field. We found that in our case the Oort cloud is a remainder originating from incomplete evaporation. In collisionally thick samples it was observed that the number of atoms can grow at the expense of the Oort cloud occupation, which is in sharp contrast to the usually presumed particle loss due to three-body recombination (see Fig. 2).

Our theoretical research was concentrated on low-dimensional and on dipolar ultra-cold dilute systems. Low-dimensional Bose systems attract a great deal of interest as they exhibit remarkable features not encountered

in three dimensions. For example, one-dimensional (1D) Bose gases with repulsive interparticle interaction become increasingly non-ideal for decreasing density. Fast progress in evaporative and optical cooling of trapped atoms stimulated a search for non-trivial trapping geometries. Present experimental possibilities allow to (tightly) confine the radial (axial) motion of atoms in a cylindrical trap to the level of zero point oscillation and thus to create 1D (2D) gases.

We have analyzed the regimes of quantum degeneracy in a trapped 1D gas with repulsive interactions between the atoms. Temperature reduction leads to a continuous transformation from a classical gas to a quantum degenerate system. We have identified 3 quantum degenerate regimes. (a) For sufficiently strong interparticle interaction and atom numbers smaller than a certain critical value, the atoms behave as a gas of impenetrable bosons with the density profile of a trapped Fermi-gas (fermionization into a trapped Tonks gas phase). For weakly interacting gases we distinguish two degenerate regimes. (b) For relatively high temperatures our calculations of the density and phase fluctuations indicate the existence of a quasicondensate, i.e. the BEC state where the density fluctuations are suppressed but the phase still fluctuates. (c) At very low temperatures the long-wave fluctuations of the phase are suppressed due to the finite size of the system (a consequence of the trapping potential), and the quasicondensate turns into a true condensate. The true condensate and the quasicondensate have the same Thomas-Fermi density profile and local correlation properties. We have analyzed how to discriminate experimentally between these two types of condensates.

Our analysis of interatomic collisions in a Bose gas tightly confined in one (axial) direction has revealed two regimes of scattering. In the quasi 2D regime, where the confinement frequency greatly exceeds the gas temperature, the scattering rates exhibit 2D features of the particle motion. At temperatures of the order of the axial frequency one has a confinement-dominated 3D regime where the confinement can change the momentum dependence of the scattering amplitudes. In both regimes the rates of elastic and inelastic collisions strongly deviate from the ordinary 3D behavior. We described the collision-induced energy exchange between the axial and radial degrees of freedom and analyzed recent experiments on thermalization and spin relaxation rates in a tightly confined gas of cesium atoms.

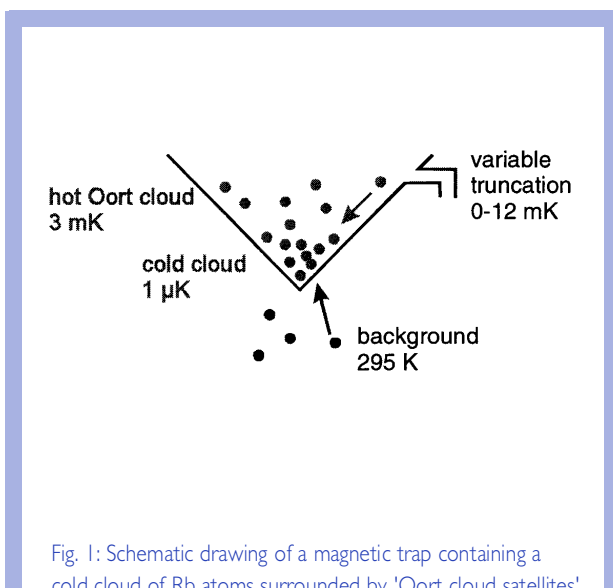


Fig. 1: Schematic drawing of a magnetic trap containing a cold cloud of Rb atoms surrounded by 'Oort cloud satellites' in the presence of (untrapped) background gas.

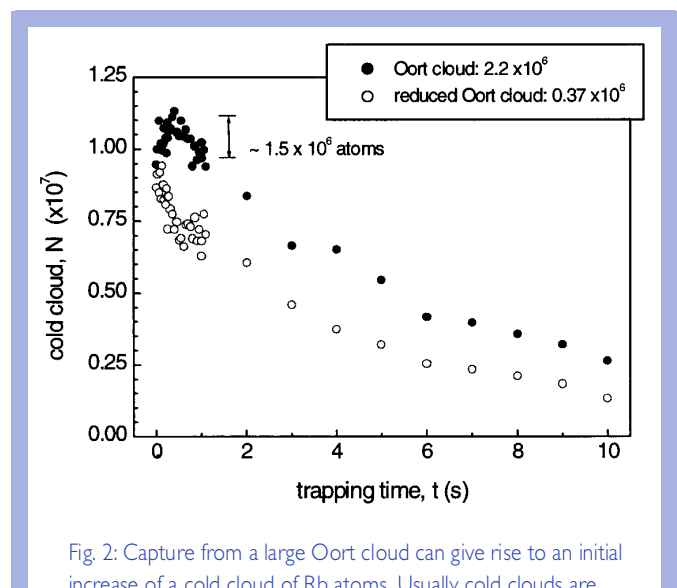


Fig. 2: Capture from a large Oort cloud can give rise to an initial increase of a cold cloud of Rb atoms. Usually cold clouds are presumed to decay due to three-body recombination.

The recent success in creating ultra-cold molecular clouds opens fascinating prospects to achieve quantum degeneracy in trapped gases of heteronuclear molecules. We proposed a method of creating a polarized atomic dipolar gas by laser coupling of the ground atomic state to an electrically polarized Rydberg state. The dipole-dipole interaction between the atoms is long-range and anisotropic (partially attractive). We have found a striking difference from common atomic condensates: In the BEC regime the sign and the value of the dipole-dipole interaction energy in the system is strongly influenced by the trapping geometry. This offers new possibilities for controlling and engineering macroscopic quantum states.

INVESTIGATORS : K. Dieckmann, I. Shvarchuck, M. Zielonkovski, W. Von Klitzing (experiment), D. Petrov, L. Vichi and G.V. Shlyapnikov (theory)

TECHNICAL SUPPORT : R. Kemper and H. Schoenmaker

G.V. Shlyapnikov is also laboratory head at the RRC Kuchatov Institute in Moscow

J.T.M. Walraven is also professor of physics at the University of Amsterdam

5.2 MOLECULAR BEAMS

A.W. Kleyn

This group studies the dynamics of gas-surface interactions by scattering beams from the surfaces and by studying surface photochemistry. In 2000 A.W. Kleyn left AMOLF to become full-time professor at Leiden University.

The interaction of low energy (0.1-1.7 eV) molecules with single crystal surfaces has been studied using molecular beam techniques. The scattered molecules are detected by a rotating quadrupole mass spectrometer. A second beam line can produce a pulsed beam of state-selected molecules. In the case of NO these molecules can be oriented in front of the sample surface.

Experiments have been carried out on the scattering and sticking of NO molecules at the Al(111) surface. This surface is chosen because oxidation of Al is still not understood. It seems that about half of the O atoms formed in dissociative chemisorption of O₂ is ejected ('abstracted') into the gas phase. To study the effect in more detail, measurements of the steric effect in adsorption of NO have been carried out. It was found that more sticking occurs when the N-end of the molecule is closer to the surface on the approach. Because it is observed elsewhere, that O-atoms preferentially stick to the surface, our results show that the NO-molecule has to rotate at the surface before dissociation can occur.

Studies on the coadsorption of CO and H showed a sticking coefficient that is essentially zero at low translational energies and rising slowly. The CO sticking is definitely lower than for NO. At Eindhoven University of Technology this behavior has been studied using density functional theory. It was found that there exists a barrier for CO chemisorption at the H-covered Ru. The barrier shows a very strong steric effect and a strong site dependence. It was found that when the CO molecule is bound to the surface the Ru atom involved is lifted by almost 0.05 nm. The state created in this way is metastable. Both theoretically and experimentally we observe phase separation. A very interesting observation is that the phase separation is

flux dependent. This suggests that there exist stable magic clusters of CO at the surface surrounded by a sea of hydrogen atoms. The apparatus has been moved to Leiden University in the middle of 2000.

The experiment POTVIS is designed to perform measurements on surface photochemistry. This year much progress has been made on testing of a molecular beam line to carry out fast beam dosing and measurements of sticking coefficients. The apparatus has been moved to Leiden University in the end of 2000.

In order to get more insight into the behavior of physisorbed films at more complex surfaces we have studied the co-adsorption of n-butane or iso-butane with CO on Pt(533). On this stepped surface a novel state appears, because the molecule can bind in two different ways near the steps. The stacking of molecules is different in the stepped surface. In case of co-adsorption both the strongly bound CO and the more weakly bound butane influence the binding of the other. CO prevents the butane from adsorbing in its most stable binding site. Butane drives CO from atop-step sites to atop bridge sites, that are stabilized because the butane screens the dipole-dipole interaction of the CO molecules.

INVESTIGATORS : B. Berenbak (Leiden University, Amsterdam), B. Riedmüller, S. Roke, H. Scheld and S. Zboray

TECHNICAL SUPPORT : F.G. Giskes

A.W. Kleyn is full professor of chemistry at Leiden University.

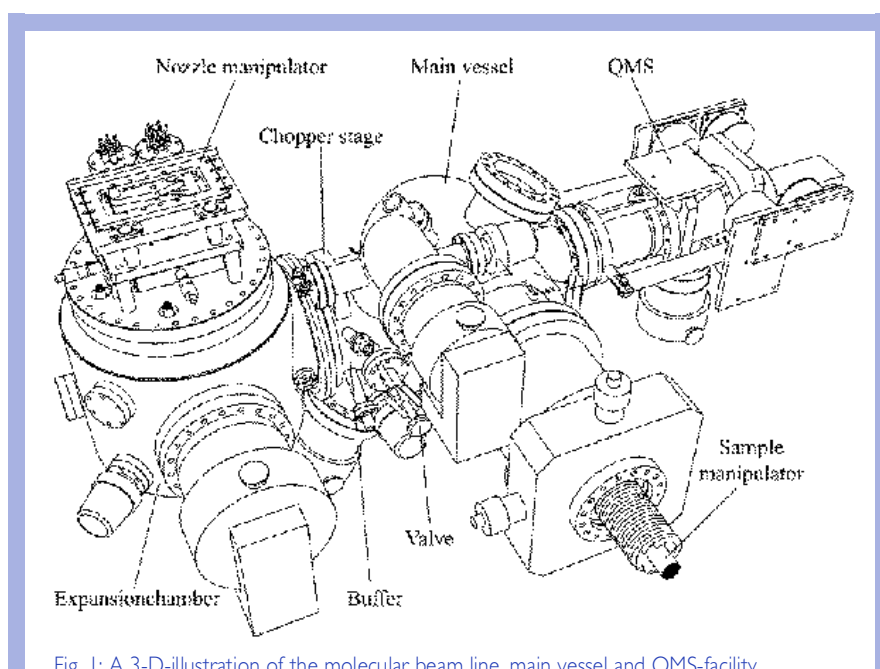


Fig. 1: A 3-D-illustration of the molecular beam line, main vessel and QMS-facility. Main vessel and sample manipulator are only drawn schematically

6. TECHNOLOGY

P.G. Kistemaker

This division consists of technological support groups, that help design, fabricate and maintain the equipment used in experiments. It also provides internet and computer support for the institute. It includes a laboratory for thin film growth, a design department, a mechanical workshop and an electronics and informatics laboratory.

6.1 THIN FILM LABORATORY

J. Verhoeven

This group supports other groups in the institute in producing thin films and sub-micron structures and conducts fundamental research in layer growth from sub-monolayer to several tens of monolayers.

GROWTH OF PALLADIUM ISLANDS ON A TiO_2 (110) SURFACE

Our project concerns an investigation of the size and shape of the islands as a function of initial deposited amount of palladium and temperature. We use a variable temperature STM as the main experimental technique, combined with mass spectroscopy, LEED, Auger electron spectroscopy and X-ray photoelectron spectroscopy. For deposition of palladium an electron beam evaporation source is available in the experimental system.

Preparation of a TiO_2 (110) surface with laterally large enough terraces was obtained by alternatively sputtering and heating at 900 K. However, oxygen deficiencies at the surface resulting in added rows could not be prevented. We deposited 0.3 Å palladium by evaporation on a substrate at room temperature. It turned out that clusters were formed during the deposition process (see Fig. 1). Mobile palladium islands with a size of 1.5 nm could be observed at room temperature. After several heat treatments the average cluster size was observed to increase. From the evolution of the cluster size distribution (Fig. 2) it could be concluded that coalescence forms the major principle in the process. We observed that the coalescence velocity for clusters on a less reduced surface is much faster than for a more strongly reduced surface. Also step decoration was observed, suggesting that oxygen defects act as pinning sites.

Testing of the new Omicron AFM / STM system was started. Atomic resolution has been achieved on a Si (111) surface by non contact AFM. Image reversion has been observed, but is not yet understood.

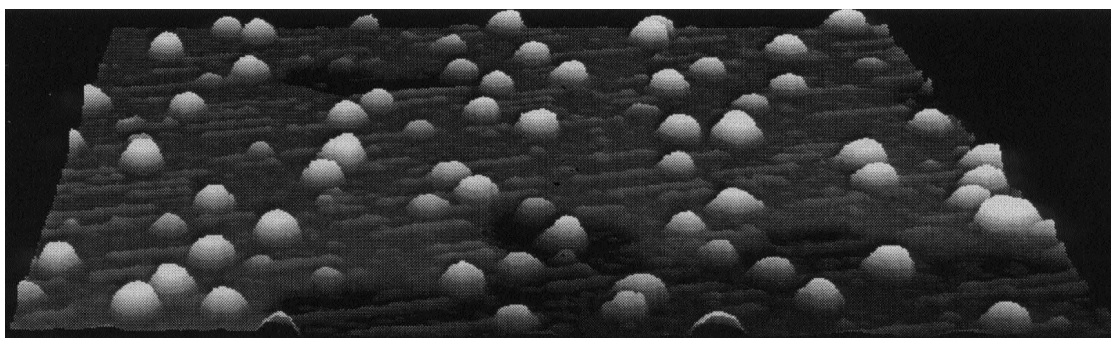


Fig. 1: STM image of palladium islands on top of a TiO_2 (110) surface.

Lateral scale is 62.5x62.5 nm

MULTILAYER SYSTEMS

This year new experiments were started for the development of multilayer systems to be applied in the 'water window' (2 - 4.4 nm). Radiation in this wavelength region is interesting for X-ray microscopy of biological samples. The advantage of this wavelength region is an improved contrast for carbon due to a high absorption. The aim is to design optics with a high reflectivity. In the past experiments were done on the Ni/Si and the Co/Si systems. We will continue to replace silicon by lithium fluoride or lithium oxide.

GENERATION OF SHORT WAVELENGTH RADIATION

It is well known that a charged particle emits Cherenkov light, when its speed exceeds the phase velocity of light c/n in a medium with refractive index n . This 'shock wave of light' is emitted at the angle of constructive interference, given by $\cos(\theta) = 1/(n\beta)$ with $\beta = v/c$ and v the speed of the particle. The Cherenkov radiation is limited to the frequency regions where the condition $n(\omega) > 1/\beta$ is fulfilled. This is mainly at near-ultraviolet, visible and longer wavelengths (see Fig. 3). Cherenkov radiation in the X-ray domain was excluded for a long time, because above the plasma frequency the refractive index is generally smaller than unity. The exceptions are the small regions of anomalous dispersion around absorption edges, where the refractive index may slightly exceed unity, but these regions were disregarded because of strong absorption.

At the exit of an accelerator a foil chamber is mounted. At this point we have the possibility to place the Cherenkov foil into the electron beam. After the foil chamber the electrons have to be separated from the photons. The electrons are bent downwards by bending magnet into a polymer irradiation beamline. At the end of that line the beam current can be measured. The vacuum chamber in the bending magnet has a triangular shape to allow detection of the Cherenkov light cone at angles up to 15 degrees (see Fig. 4).

SUPPORT ACTIVITIES

The group produces a wide variety of thin films for research groups at AMOLF and other institutes and universities. Scientists from outside often take part in the deposition process or even operate the deposition systems themselves to produce layers for their own experiments. Various techniques are available for the production of tailor made thin films: sputter deposition, ion assisted deposition (evaporation), and low energy ion beam modification (< 1000 eV) of thin films. This year also activities to introduce lateral structures into thin films were started. This work is mainly performed at DIMES (E. van der Drift). An important application will be the fabrication of a transmission grating to separate higher harmonics of short wavelength lasers (XUV group).

INVESTIGATORS : H. Hopman, J. Chrost, M. Jak, M. Kessels and J.W.M. Frenken (Leiden University)

TECHNICAL SUPPORT : H. Zeijlemaker and M. van den Boer

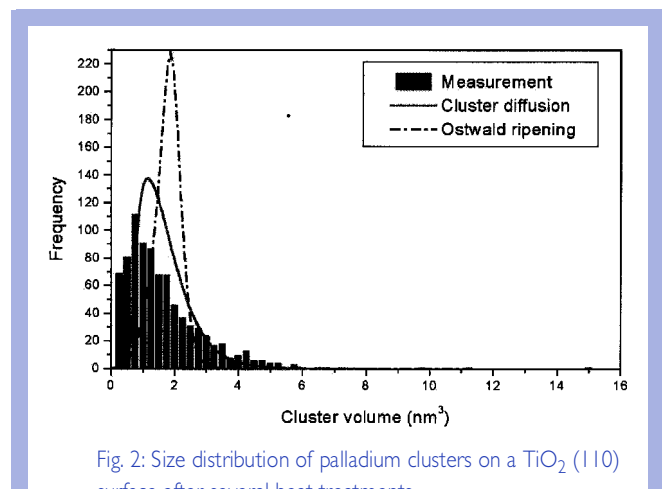


Fig. 2: Size distribution of palladium clusters on a TiO_2 (110) surface after several heat treatments

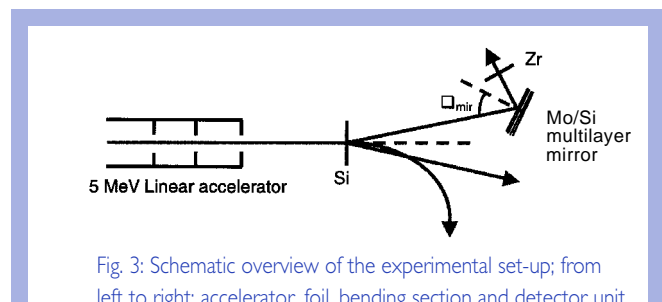


Fig. 3: Schematic overview of the experimental set-up; from left to right: accelerator, foil, bending section and detector unit.

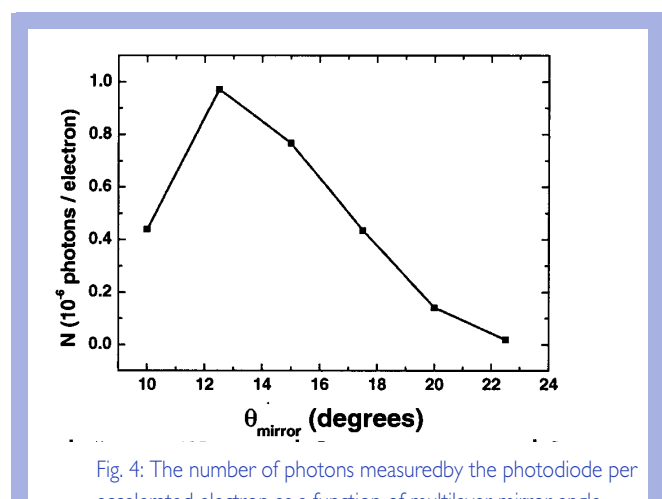


Fig. 4: The number of photons measured by the photodiode per accelerated electron as a function of multilayer mirror angle.

6.2 ELECTRONICS AND INFORMATICS LABORATORY

C.B. Okhuijsen

The services of the electronics and informatics laboratory (E&I) are directed towards technical support for the entire institute. In this respect, the results of E&I's efforts are visible in almost all experiments and on every desktop. Representative examples of our work are listed below.

ELECTRONICS AND SOFTWARE ENGINEERING

The applicability of LabVIEW as a general-purpose tool for experiment control and measurement continues to grow. For almost all new projects LabVIEW now is the first tool considered. We started a discussion list of users through e-mail; it currently contains more than 20 subscribers within AMOLF.

The development time of a typical software project is increasing because the users ask for a more extended user interface. As a result, our attention was mostly focussed to a few larger projects.

PROJECTS COMPLETED IN 2000:

- Synchronous signal generator for XUV physics
- Framegrabber based on micro-enable hardware for XUV physics
- Monocyclic pulse generator for vibration dynamics
- Control of the high harmonics laser
- Nozzle controls for molecular beams
- Measurement and control program for the FTICR experiment
- Trap switch for FTICR
- Arbitrary Waveform Generator / Transient Digitizer
- Program for the bio-organization group based on IDL
- 4-Quadrant pre-amplifier for bio-organization experiment
- Stepper motor controls for order/disorder (SAXS)
- LabVIEW application program for order/disorder experiment
- Event timing analysis program for order/disorder experiment
- 1 MHz quadrupole power supply for complex fluids experiment
- 36-Node PC cluster for computational physics group
- Dynamic wafer-curvature/stress measurement for ion implanter
- Hard- en software for the WAXS detector in Grenoble (DUBBLE)
- Power and flow control for quantum gas experiment
- Glasfiber HotLink based on Micro Enable board for the NACRA microscope
- Magnetic key control program

NETWORK AND SUPPORT

A new router was extended to also serve as the backbone of our institute, and the bandwidth to connections outside AMOLF grew from 10 MB/s to 2 GB/s. Macintosh support was discontinued, and a number of file servers was installed. The modem-pool was updated.

PERSONNEL : H.P. Alberda, I.A. Attema, H.A. Dekker, N. Dijkhuizen, C.J. van Doornik, D. Driessen, J.N. van Elst, J. ter Horst, M. Konijnenburg, S. Kossen (trainee), R. Schaafsma, M. Seynen, D.J.P. Verheijde, A.J.M. Vijftigschild, J. Vink (trainee) and S.W. Wouda.

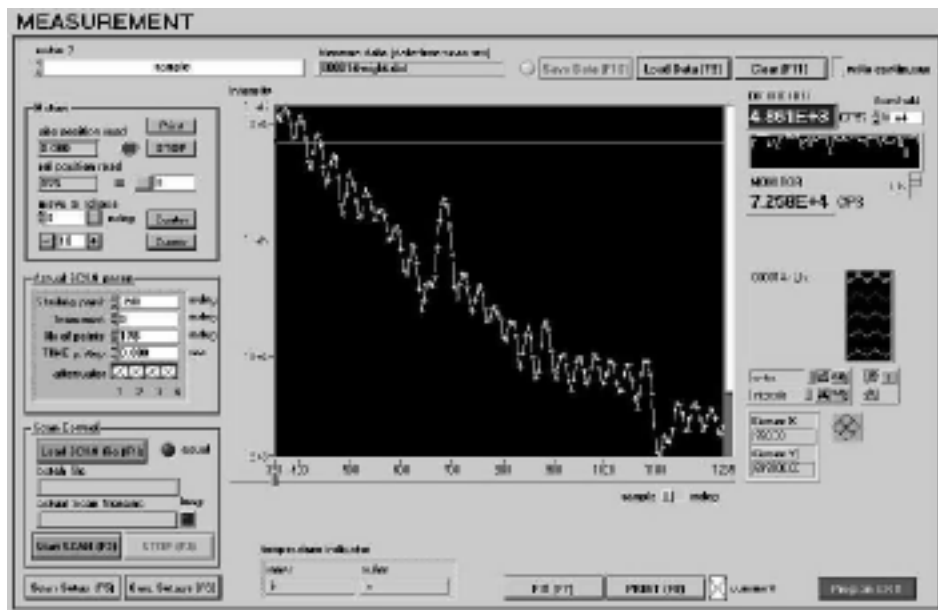


Fig. 1: LABView display for REFLECTIVITY application

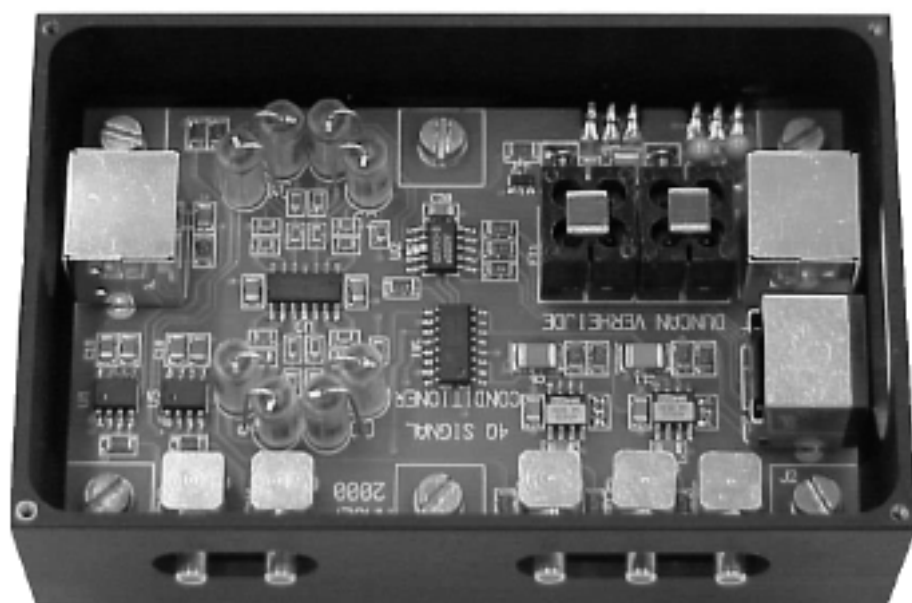


Fig. 2: 4-Quadrant signal conditioner

6.3 COMPUTER AIDED ENGINEERING DEPARTMENT

D. Glastra van Loon

The computer aided engineering (CAE)-department produces mechanical designs of scientific equipment and advises the scientific groups and the research technicians on mechanical construction.

Five workstations are available for Computer Aided Engineering (CAE). We use the I-DEAS Master Series[®] software from SDRC for tasks such as solid modeling, system assembly, automatic generation of workshop drawings and mechanism analysis. Also finite element analysis, such as the determination of natural frequencies, heat transfer and other physical behavior, can be done.

In 2000 we switched from the Unix operating system to Windows NT-workstations. The new software release gives us more flexibility in switching between the 2- and 3-dimensional design facilities and is fully windows-native.

MAIN DESIGN -ACTIVITIES IN 2000:

- Several design activities for a XUV-spectrometer (M. Vrakking):
 - spherical stage for a droplet source nozzle
 - cluster source
 - filter carousel
 - pulsed valve with iodine injection
 - time-of-flight spectrometer
 - several vacuum chambers
- Complete design of a field induced recombination experiment (B. Noordam);
- Customized sample stages, objective holders and other special components for optical trap microscopy (M. Dogterom, and A. van Blaaderen)
- Redesign of a piezo-based sample drive for scanning tunneling microscopy (J. Verhoeven)
- Modification on the DUBBLE H-line monochromator at ESRF
- Design of a biased junction multi channel plate detector (W. van der Zande)

The CAE-department also supports the scientists with the realization of conference posters.

PERSONNEL : I. Cerjak, J. van Dorsselaer
and D.J. Spaanderman

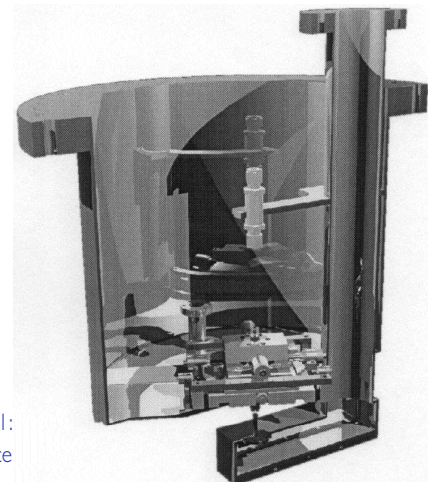


Fig. 1:
Artist's impression of the XUV droplet source

6.4 MECHANICAL WORKSHOP

W.H. Brouwer

The mechanical workshop makes equipment for laboratory experiments. Tools are available for machining, diamond cutting, vacuum brazing and welding of materials. Three milling machines and a wire electrical discharge machine are computer controlled and are linked to a programmable central workstation. Drawings from the engineering office can be sent to this workstation through a direct link. An important function of the workshop is the training of apprentices in precision production.

EXAMPLES OF EQUIPMENT MANUFACTURED IN 2000:

- For the group Vibrational Dynamics essential elements for performing time-resolved experiments in the mid-infrared were made. In particular, a nitrogen flow-box, alignment slits and a rotating sample-celholder were constructed.
- A number of sources have been constructed for the XUV Physics Group, which will be used as laser plasma sources for X-ray generation, among which is a droplet source in which microscopic waterdroplets are formed using a vibrating capillary tube.
- A combined high-order harmonic generation set-up and a streak camera to monitor the time evolution of two-electron wavepackets in atoms.
- A double Penning trap holding both electrons and positive ions. The apparatus is a prototype for the trap at CERN to make antihydrogen.
- A second variable temperature, open-ended ICR-cell, suitable for temperatures below 0°C, is under construction. This cell will enable extremely refined controlled blackbody infrared dissociation and pump probe experiments on large biomacromolecules.
- A major effort for the group Order/Disorder in Soft Matter has been the completion of the building of an apparatus for Small Angle X-Ray Scattering (SAXS). In addition improved sample supports or freely suspended smectic films have been realized
- A small, but highly effective, model of two neighbouring base pairs in the DNA molecule, allowing researchers from the Theory of Complex Fluids group to sharpen their intuition on the relative degrees of freedom in the molecule
- Several components were made for the time-shared optical tweezers array that has been implemented on a confocal microscope.
- For the optical tweezers set-up a frame was made that accommodates both a spring loaded manual stage and a computer controlled piezo stage.
- A new sputter ion source for the MEV ion implanter was fabricated. Several modifications compared to an existing type were made, and lead to improved beam current. In addition, ion source cathodes of a large variety of source materials were spark-cut.

PERSONNEL : W.J. Barsingerhorn, R. Boddenberg, M.M.J.H. Borsboom, S.M.A. Kraan, J.J. van der Linden, H. Neerings, J. Smit, H.P. Vader and M.J.A. Witlox.

**7. ADMINISTRATIVE
AND
TECHNICAL SUPPORT**

P.G. Kistemaker

This division combines groups that are responsible for financial administration, personnel management, secretariat and library, as well as public relations and conference organization.

7.1 FINANCIAL ADMINISTRATION, PERSONNEL MANAGEMENT, LIBRARY AND SECRETARIAT

P.G. Kistemaker, J.F. Stiel, W.C. Harmsen, S. Windhouwer, H.J.J.M. Lammers

The financial administration, including ordering of goods, checking invoices, charging the proper budgets and project administration is performed by the purchase department and the financial administration. The bookkeeping is executed on a central computer for the whole FOM organization. Although monthly reports provide accurate information to the budgetholders, the realization of online information is our goal.

Quarterly financial reports are introduced as a management information tool for FOM. The Institute is financed by budgets allocated to programs. Therefore costs of technical and general support are billed to the programs. This requires a time-registration of the support departments. Some 40 % of the AMOLF budget is financed by special contracts. The percentage of national (NWO) and EU contracts is growing, whereas contracts with industrial research laboratories have decreased substantially.

Personnel management is continuously changing to more individual arrangements. This reflects the wish to better synchronize the institute and private obligations. Because of the decreased interest of Dutch students for physics and chemistry, many new PhD students come from abroad. Assistance in finding housing and in the adaptation to Dutch regulations require a major effort. About 50 new employees entered the institute to take over the work of departed employees who continued their careers elsewhere. The main part of this flux consists of young scientists and technicians who finished the training on their first job. About 20 guest-scientists from countries all over the world came to the institute for a stay of a few weeks to some months. Supported by European scholarships an increasing number of postdocs from the different European countries work at AMOLF. Also many PhD students who graduated at AMOLF have obtained an EU-fellowship and have spent a year or two in another European institute.

The Information Service Department includes library services, building and maintenance of the AMOLF web site and database building. The librarians are specialized in providing the scientists with appropriate information by means of books, journals, international databases and through contacts with other libraries. The AMOLF web site is an important source of information for internal and external users. Therefore much effort is invested in continuously updating and extending the site.

Management support for the director and program coordinators, as well as the personnel - and the public relations departments are carried out by the secretariat. In addition all regular and electronic mail is handled, and agenda's are managed.

This year the secretaries had a big job in updating the address data base, and in lending support to the national and international workshops that were organized in cooperation with the public relations department.

Personnel: C.M. van Es, W. van der Kaaij, E.B. Sputneset, K. Bonsink, I.R.M. Wijne and D.M.G. Hoogesteijn.

7.2 TECHNICAL SERVICES (FACILITY MANAGEMENT)

H.H. Kersten

Five groups are involved with the care of the housing and technical facilities of the institute.

- The group Technical Services maintains the physical plant. For the major items we have a long-term plan (10 years, updated in April '99), financially supported by NWO. Another important task for this group is the preparation and installation of the connections for new experiments. Moreover, Technical Services provide the essential guard duty in the evening and the weekend for the physical plant and unattended, working, equipment.
- The group Civil Services performs cleaning and maintenance of the rooms and the building. Most of the work is done on a basis of one-year planning. The management of the cafeteria is another activity of this group. A special task for the leader of Civil Services is the allocation of the rooms to the employees of the institute.
- The Purchasing Group orders and receives the goods, and manages the stock. In stock we have about 1700 different items in a wide range from bolts to pencils and lecture bottles to connectors.
- In the Printing shop the large volume copy work is done. Besides this, information and help is provided for making posters, photographs, overhead sheets and DTP using PhotoShop and Quark XPress.
- At the reception desk the receptionist takes care of connecting phone calls, sorting incoming mail, telefaxes and the presence registration.
- Assistance with finding a living place in Amsterdam for our constantly changing group of foreign guests takes a lot of time and ingenuity. Together with arranging foreign business trips for our staff it is a full time job.
- One of the tasks of the facility manager is taking care for the safety in the institute. The institute has an automatic fire alarm system and an emergency group of about 19 people. They are skilled in first aid, fire extinguishing, evacuation and accident prevention.

ACTIVITIES

The groups Technical Services and Civil Services have a valuable task in internal moves and renovations in the institute. This year some of the topics were:

- Upgrading the air conditioning system in the laser laboratory: two new compressors instead of one (back up), better air filters (class EU7) and a new high capacity air cooler (70 kW instead of 50 kW). To bring in the fresh air we try out "air hoses" instead of the normal exhaust grids.
- Two experiments from the main hall were moved to the University of Leiden, so the chance was taken to shuffle other experiments in order to make a better use of the ever limited space.
- We made plans for a new, temporary building, having 25 workrooms. This will solve the structural shortage of office space from summer 2001.
- In between plans are made for building a complete new building. It will be situated between the old building and the railway. We hope to realize this plan within 5 years from now.

On and around the Science and Technology Center Watergraafsmeer, more participants have plans for new buildings. In November 2001 one will start building a new road, connecting the Molukkenstraat with the Kruislaan, so making this region more accessible. We participate in a few coordination teams (e.g. energy management, parking management, new buildings) to steer these developments and to stay in touch.

PERSONNEL : H. Bar, A. Dijkslag, I. Snel, E. Kruller, J. Heshof, H. Ackema, S. Jangbahadoor, H. de Jong, W. de Jong, Y. de Koning, G. Kroll, J. van der Loo, C. van der Meer, A. Post, M. Wennekes, G. van der Wijk, M. Witlox, H. Sodenkamp, T.W.J. zur Kleinsmiede, M. Roos, E.G. Steunebrink and M.L. Ter Stroot.

7.3 PUBLIC RELATIONS AND CONFERENCE ORGANIZATION

L. Roos and H.J.J.M. Lammers

This group focuses on all aspects of public relations activities and information to the public. Major tasks for the public relations team are the organization of tours for internal and external groups, the production of brochures, visitors guide, annual report, calendar of events, newsletters and audio-visuals. The team organizes in collaboration with other AMOLF (scientific and support) groups special events, such as farewell receptions, the open house festival, meetings and conferences. There is a fruitful collaboration with communication officers of FOM, NWO, the Dutch Universities, and AMOLF neighboring institutes of the Science and Technology Center.

An extensive project in the year 2000 was the production of a video for new AMOLF colleagues and potential co-workers. The video team was composed of B.M. Mulder (science), H.D. Alberda (technique) and H.J.J.M. Lammers and L. Roos. We trust that with this renewed public relations tool AMOLF will continue to show its attractive and positive aspects to those who have just landed or will join the Institute.

Several international and national workshops and meetings were organized during the year i.e. the Huygens Symposium on Quantum Gases, the Fourth Infrared User's Group Meeting (IRUG4) in Conservation Science, the Meeting of the EU POLYNANO-project and the EU-network meeting on Electron Transfer Reactions.

The year 2000 calendar of events, available on the AMOLF website, contained a variety of activities.

JANUARY

- 3 New Year's gathering
- 21 Inaugural lecture Bart Noordam (Free University of Amsterdam)
- 28 Meeting of the Research Policy Board AMOLF

FEBRUARI

- 14-18 Fourth Infrared Users' Group Meeting (IRUG4) in Conservation Science (Bonniefantemuseum of Maastricht)
- 15 Skating activity and 'snert' (personnel club)

MARCH

- 9 Excursion by students of the Technical University of Delft
- 14 Visit of the NWO-Groot Apparatuurcommissie
- 31 Inaugural lecture Wim de Jeu (Technical University of Eindhoven)

APRIL

- 7 Festivities for H. Bar (25 years employment at FOM)

MAY

- 11 Sports activities and Oriental dinner (personnel club FOM Foundation)
- 26 Congress Quantum-Electronics Symposium on Femtophysics of Condensed-Phase Systems (Amsterdam)

JUNE

- 14 Celebration Jaap Sanders' birthday (70 years)
- 20 Visit of a NWO delegation
- 21 Tour for teachers of the Plein college Sint Joris (Eindhoven)
- 30 Inaugural Lecture Aart Kleyn (University of Leiden)

JULY

5 Excursion for all AMOLF personnel to Texel (personnel club)

SEPTEMBER

18-19 Meeting of the EU POLYNANO-project (Oud-Poelgeest, Leiden)

20 Meeting of the Research Policy Board AMOLF

OCTOBER

8 Open House Event for the public and children's Fun Lab

19 Farewell reception for Bart Noordam

30 Visit of a NWO delegation

NOVEMBER

5 Party for Daan Frenkel (Spinoza Award)

7 NWO/Huygens-lecture on Bose-Einstein Condensation, a New Form of Matter at a Temperature near Absolute Zero, by C. Wieman and reference lecturer J.T.M. Walraven (Den Haag)

8 Huygens symposium on Quantum Gases (Amsterdam)

9 Excursion for foreign employees: Science in Amsterdam in the beginning of the 20th century (personnel club)

24-25 EU-network meeting on Electron Transfer Reactions (Lorentz Centre, Leiden)

DECEMBER

5 Sint Nicolas Celebration (personnel club)

11 Excursion for new employees of the FOM Foundation

12 Farewell reception for Aart Kleyn, Heiner Scheld and Bart Berenbak

21 Christmas colloquium and lunch (personnel club)

The PR activities were supported by members of the technical, household, administrative and secretarial groups, especially by D.M.G. Hoogesteijn, H. Sodenkamp and R. Kemper.



The christmas lunch, as always organized by the personnel club, turns out to be a bigger event every year. This year we all had lunch in an oriental atmosphere.

